Energy Materials Challenges

Theory and computation for Interface Science and Catalysis

Cynthia Friend

Harvard University

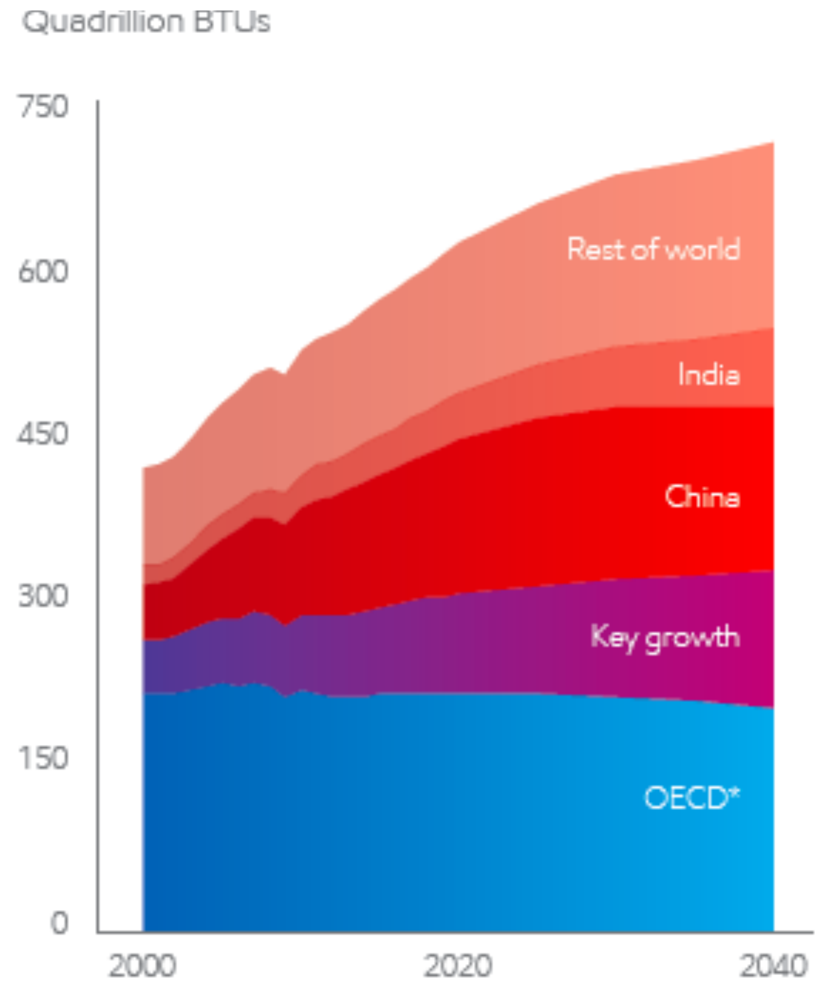
Integrated collaboration between theory and experiment

Tim Kaxiras

Alex Tkatchenko

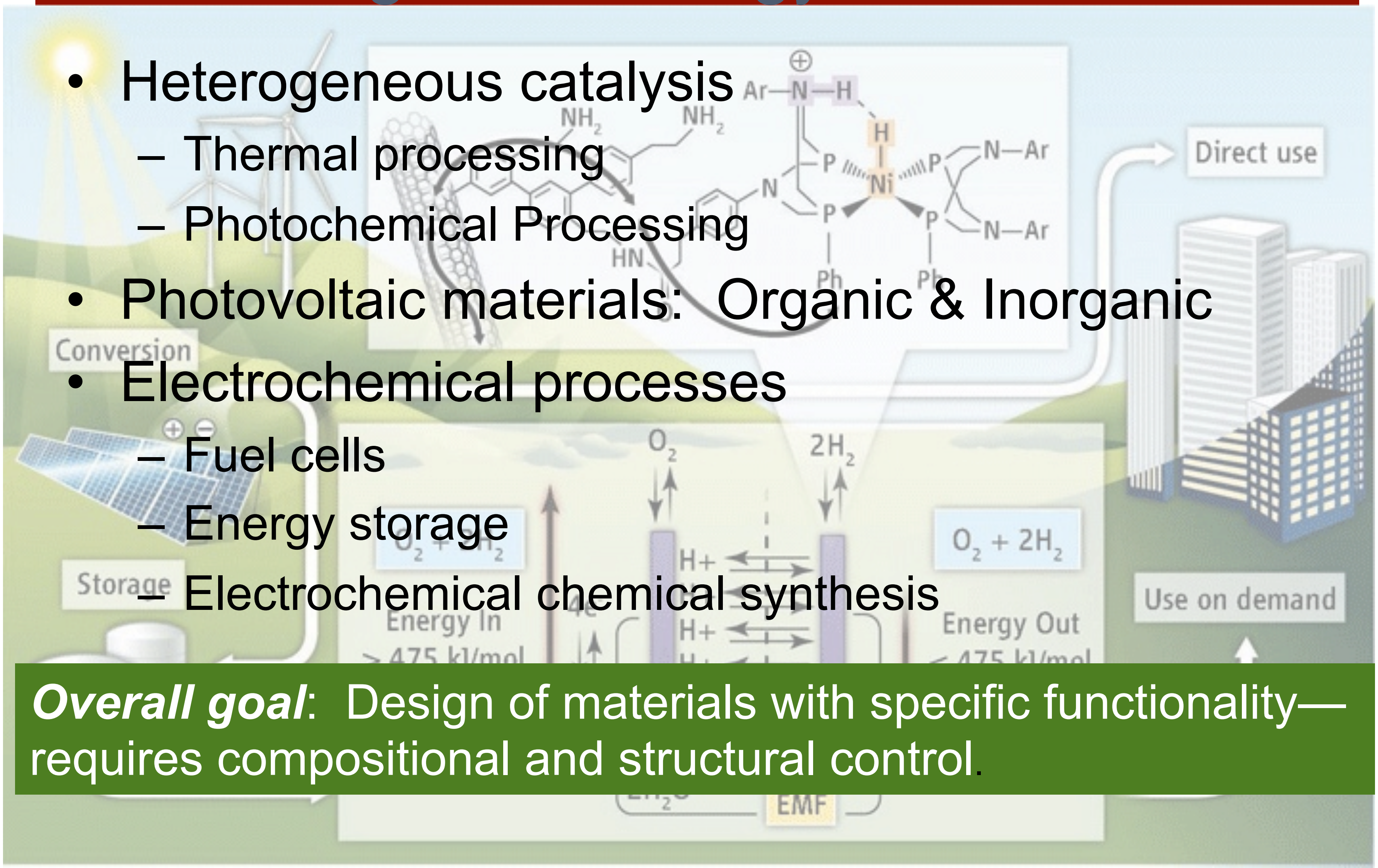
Energy outlook for 2040

- 2 billion more people
- 130% larger global economy
- ~35% increase in demand for energy or more than 100% increase without efficiency gain
- 90% growth in demand for electricity



EXXONMOBIL, "The Outlook for Energy 2040" (2014).

Many materials and processing challenges for energy research



- Heterogeneous catalysis
  - Thermal processing
  - Photochemical Processing
- Photovoltaic materials: Organic & Inorganic
- Electrochemical processes
  - Fuel cells
  - Energy storage
  - Electrochemical chemical synthesis

Overall goal: Design of materials with specific functionality—requires compositional and structural control.

Key points to consider in modeling of energy-related problems

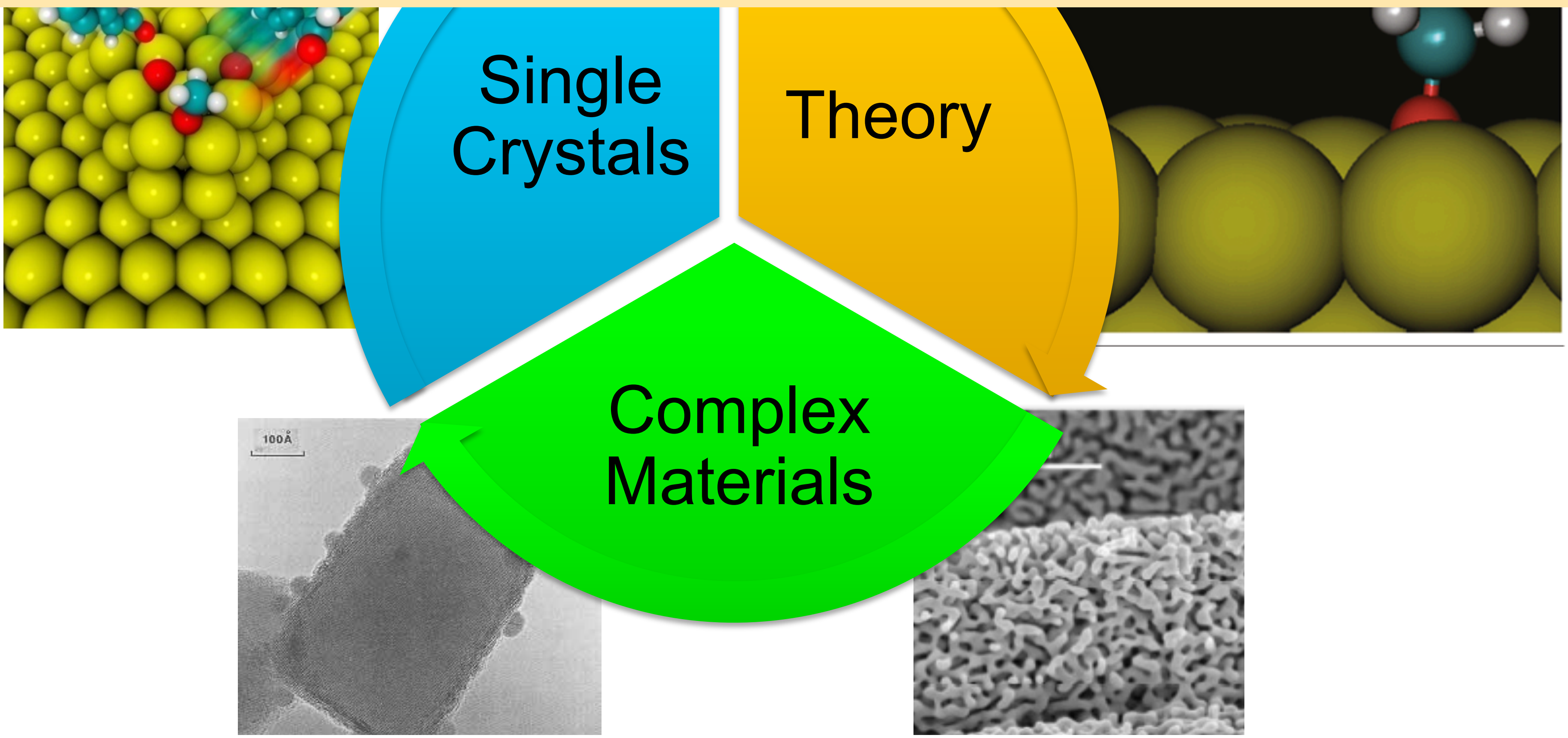
- Set up simplified models and use experimental information as a guide
- Add complexity to test for importance
  - Surface reconstruction or metal atom release
  - Compositional variation in, e.g. oxides or sulfides
- Molecular systems require inclusion of weak (van der Waal's) interactions
- Kinetic modeling important for many processes
- Photon-driven processes require treatment of excited states and time-dependent models

Examples of experimental benchmarks

- Spectroscopy
  - X-ray tools (e.g. XPS, XAS, XES, EDS)
  - Vibrational spectroscopy (IR, Raman, HREELS)
- Imaging
  - STM/AFM; TEM, SEM
- Structural probes (averaging)
  - Diffraction; Scattering, e.g. EXAFS
- Reactivity measurements/Rate measurements

Enhancing Energy Efficiency:The Power of Fundamental Studies

Fundamental need: To design new, efficient catalytic processes based on understanding of bonding and reactivity.



Thermal Catalysis: Modification of kinetics via introducing intermediate steps

- Increase ***rate***
- ***Lower*** operating ***temperature*** (save energy)

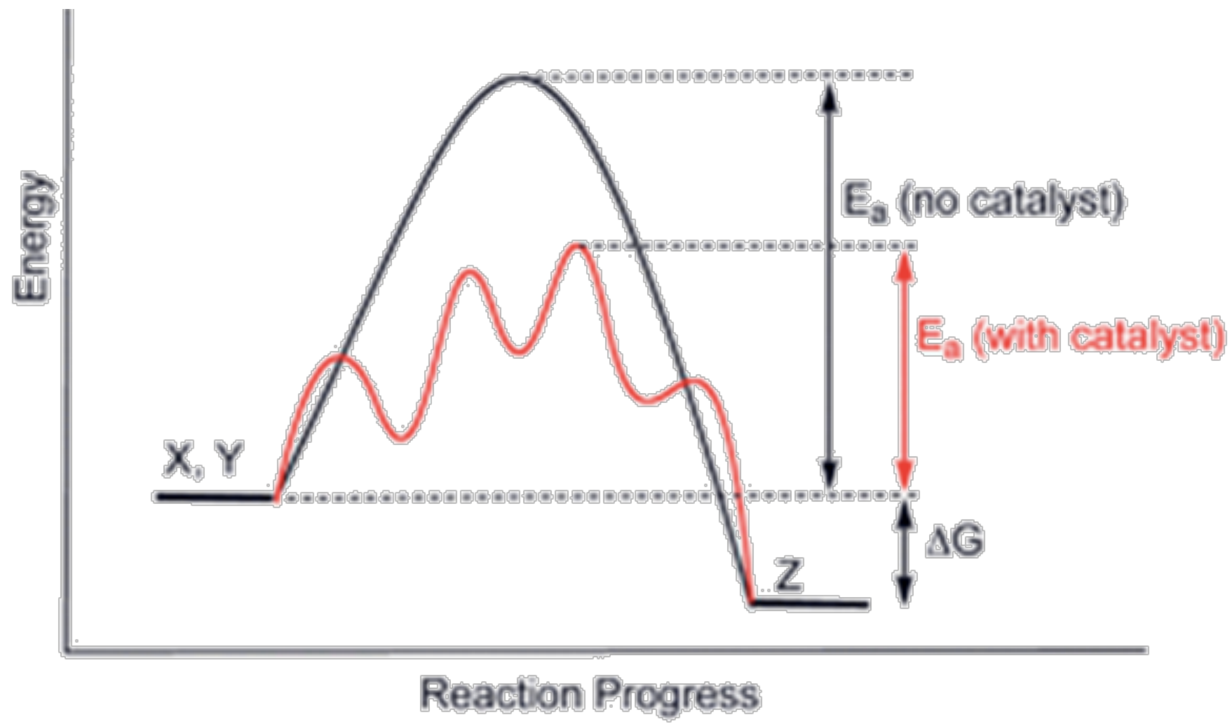
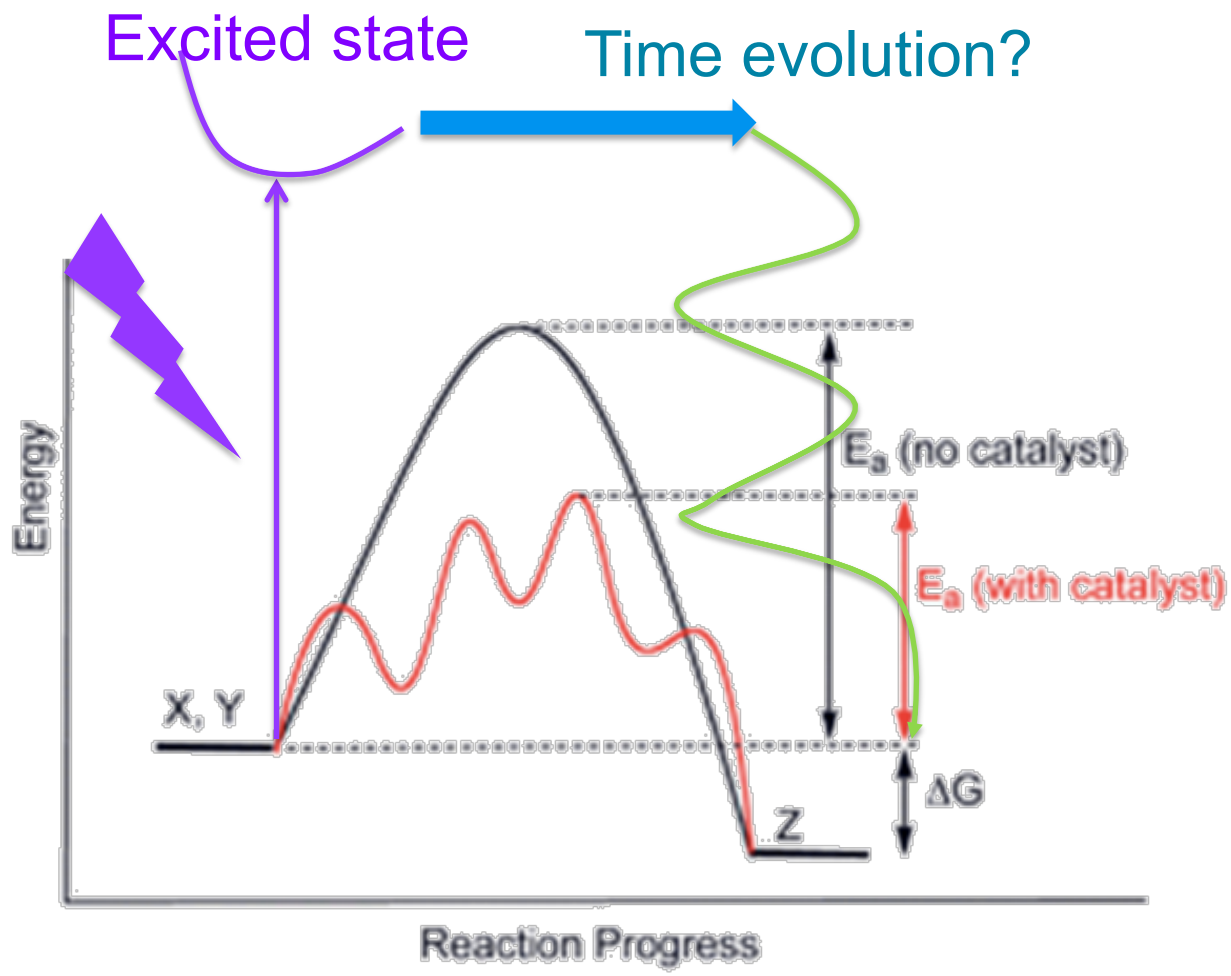
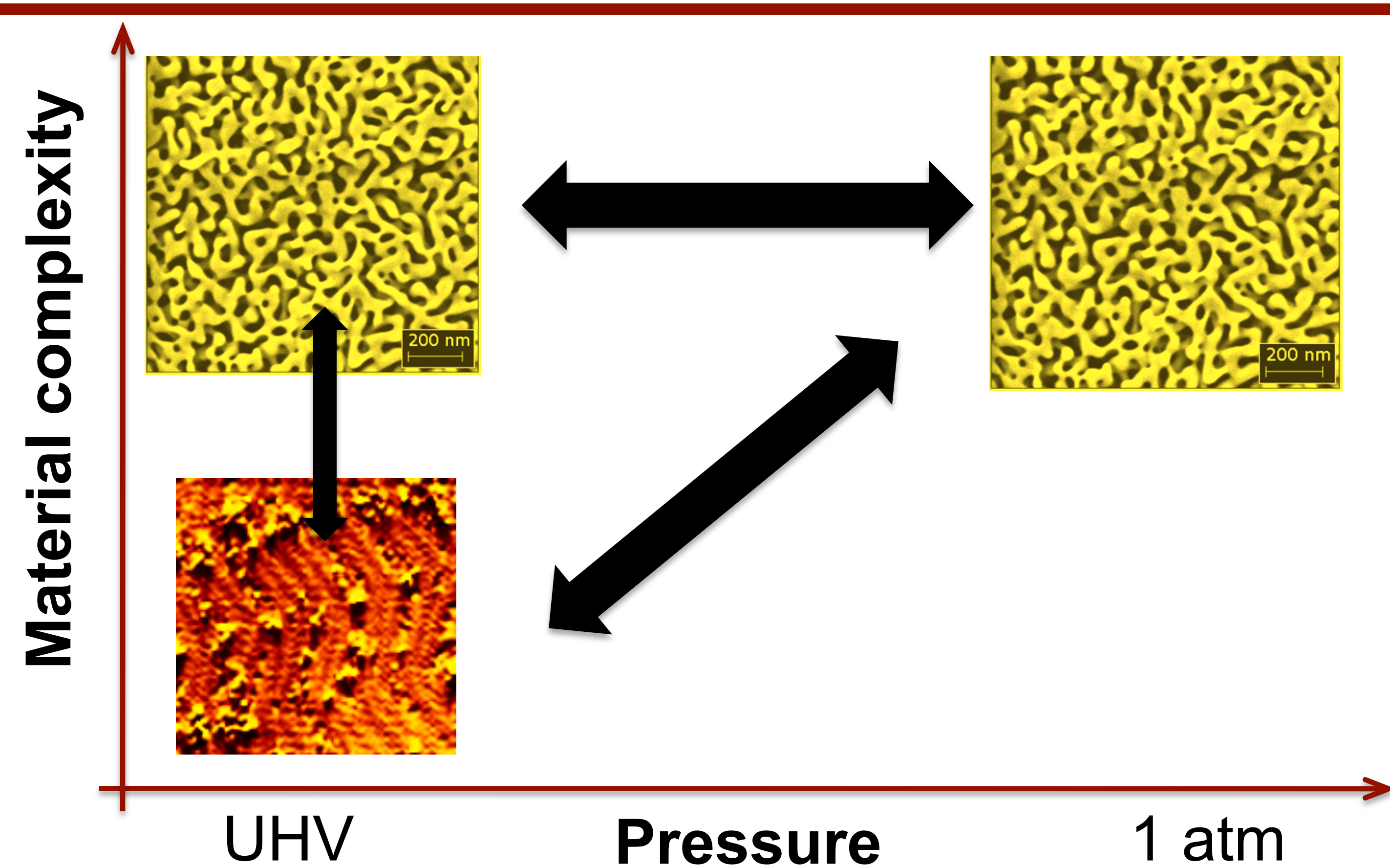


Photo-catalysis: Modification of kinetics by accessing excited state

- Increase ***rate***
- Drives reactions, even uphill reactions, using light

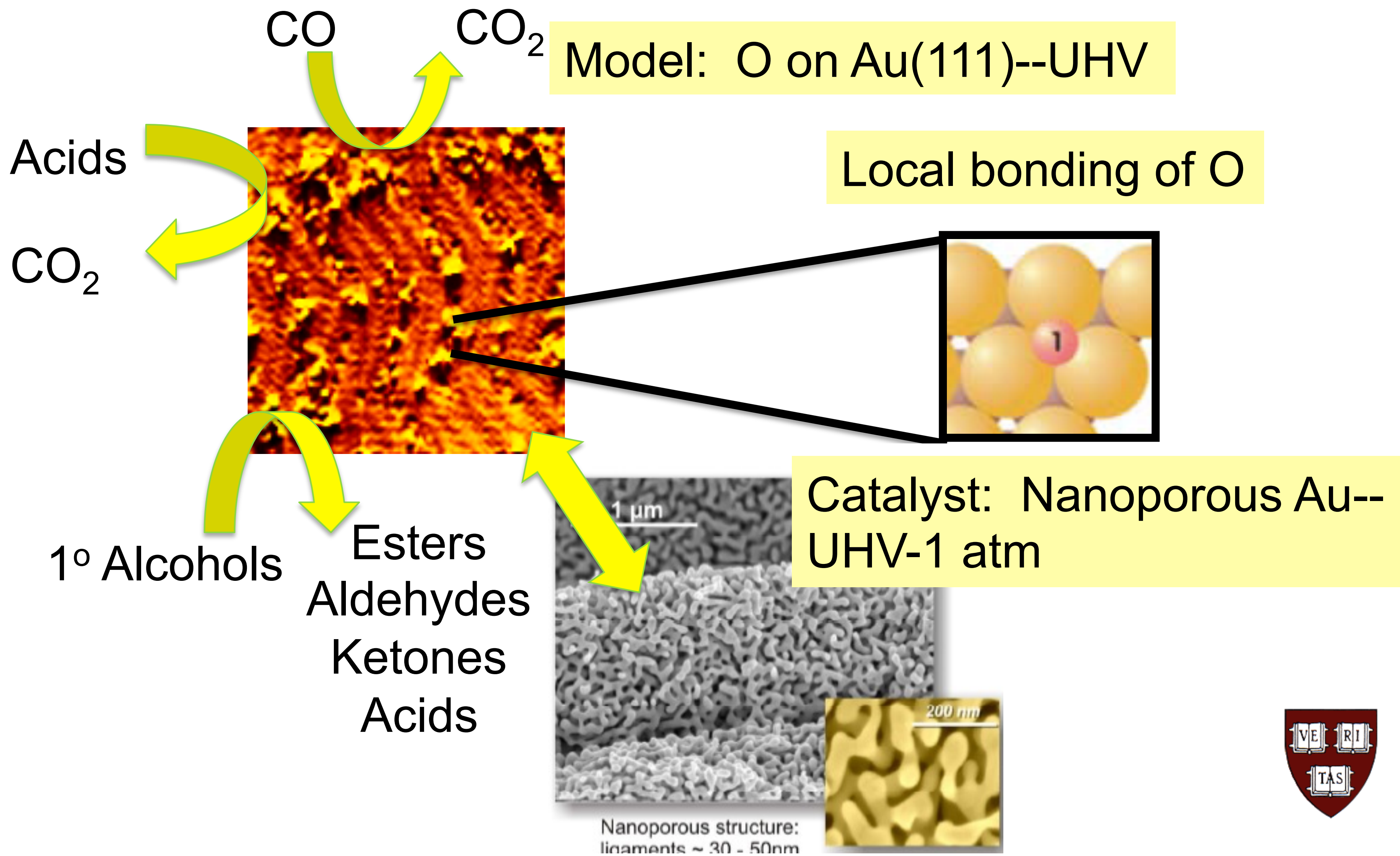


Bridging materials' complexity and pressure



Well-defined conditions yield molecular level understanding and bridge to theory

Multiscale modeling of selective oxidation of organics by gold: Single crystals and nanoporous materials



Key insights from fundamental studies:

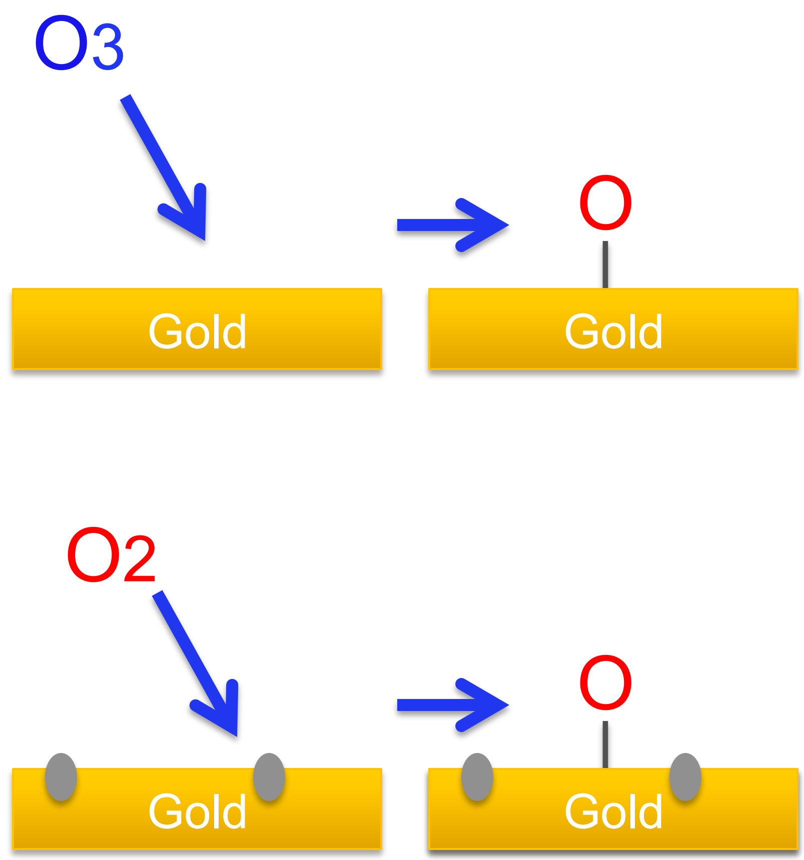
- Catalytic performance at 1 atm. predicted from fundamental surface chemistry
- Mechanistic framework used to ***predict*** new reactions
- Understanding hierarchy of bond strengths that determine coverage in complex reactive environments
- Catalyst activation: Metastable surface structures are key to activity and selectivity

Critical reactive step: $O_2 \rightarrow 2\ O_{ads}$

Metallic Au does not dissociate O_2 efficiently

Our approach:

1. Study O/Au by using other sources of O_{ads}
2. Investigate materials with minority active component for O_2 dissociation, e.g Ag; migration (spillover) to Au leads to reaction



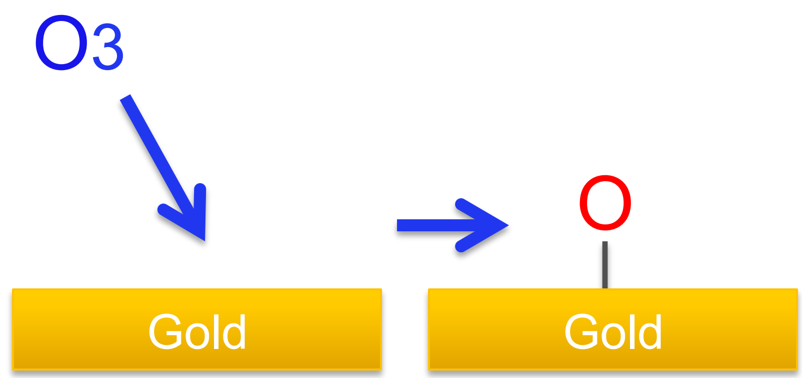
Oxide supports are also a source of O_{ads}

Critical reactive step: $O_2 \rightarrow 2\ O_{ads}$

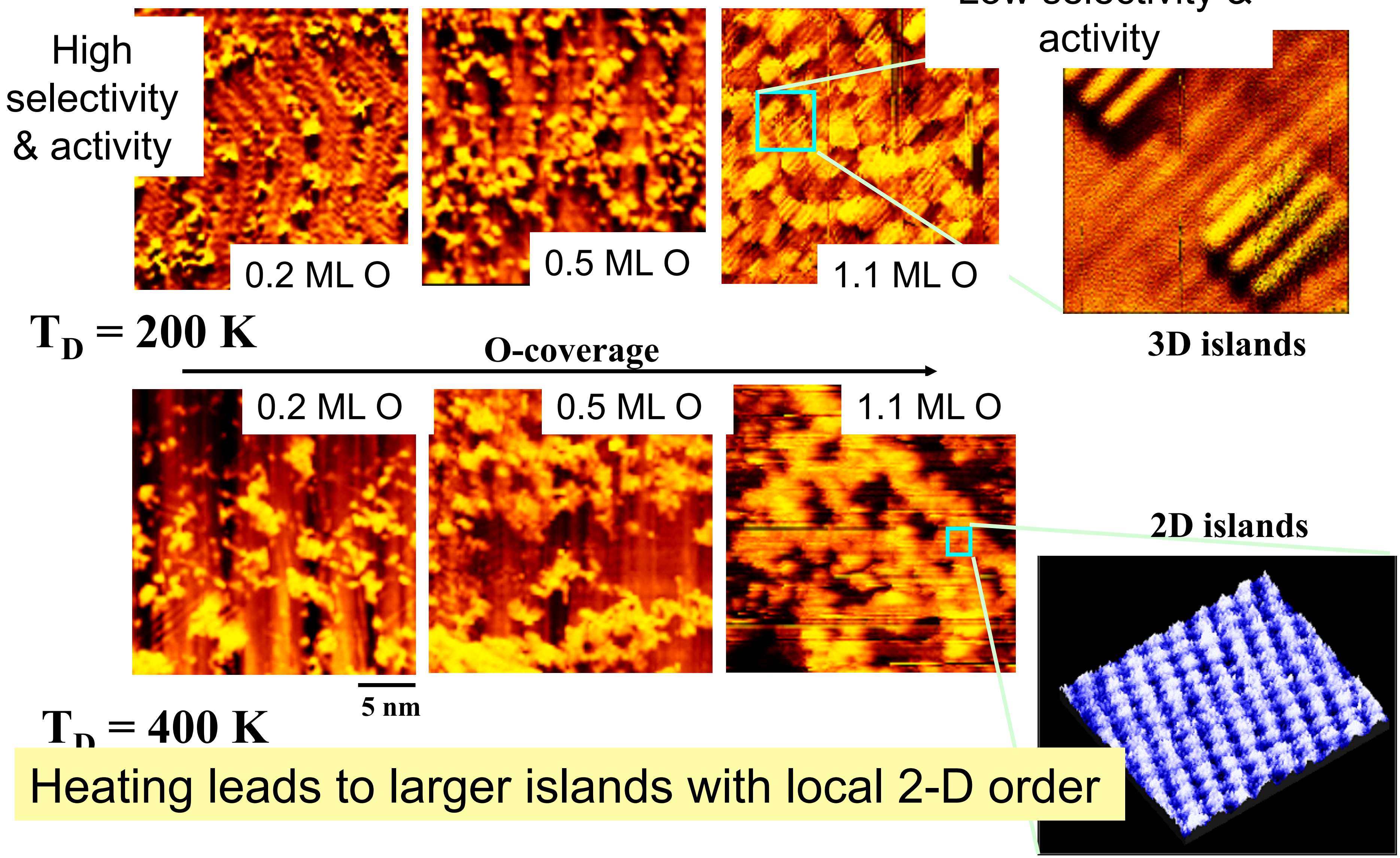
Metallic Au does not dissociate O_2 efficiently

Our approach:

1. Study O/Au by using other sources of O_{ads}

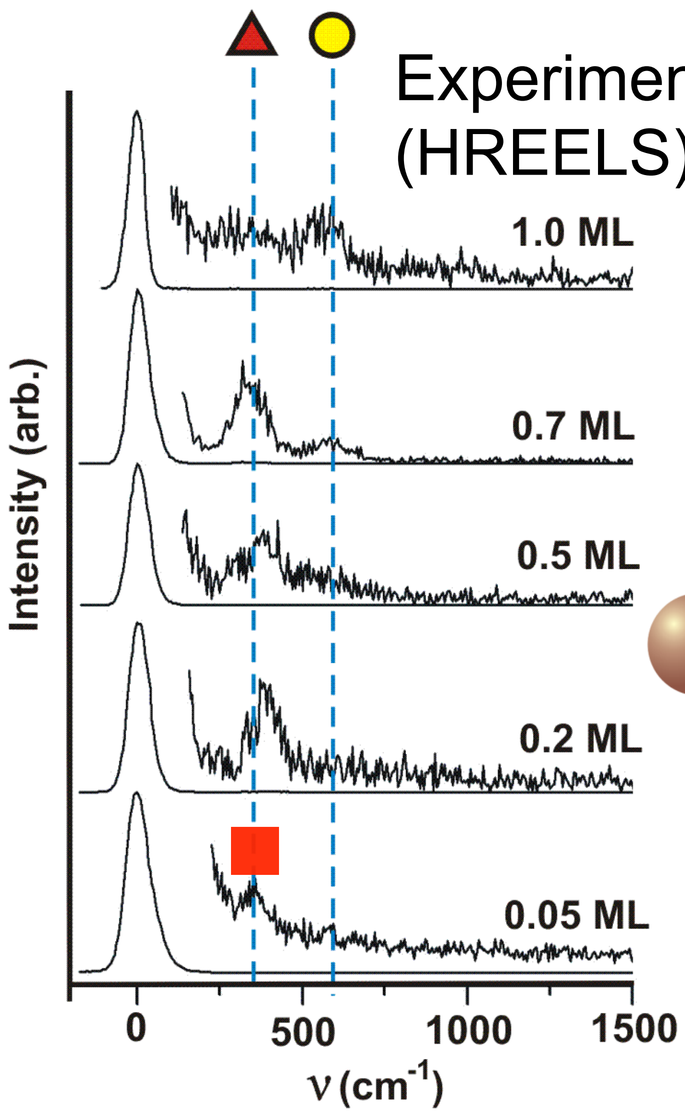


Metastable nanostructures have high reactivity & high selectivity



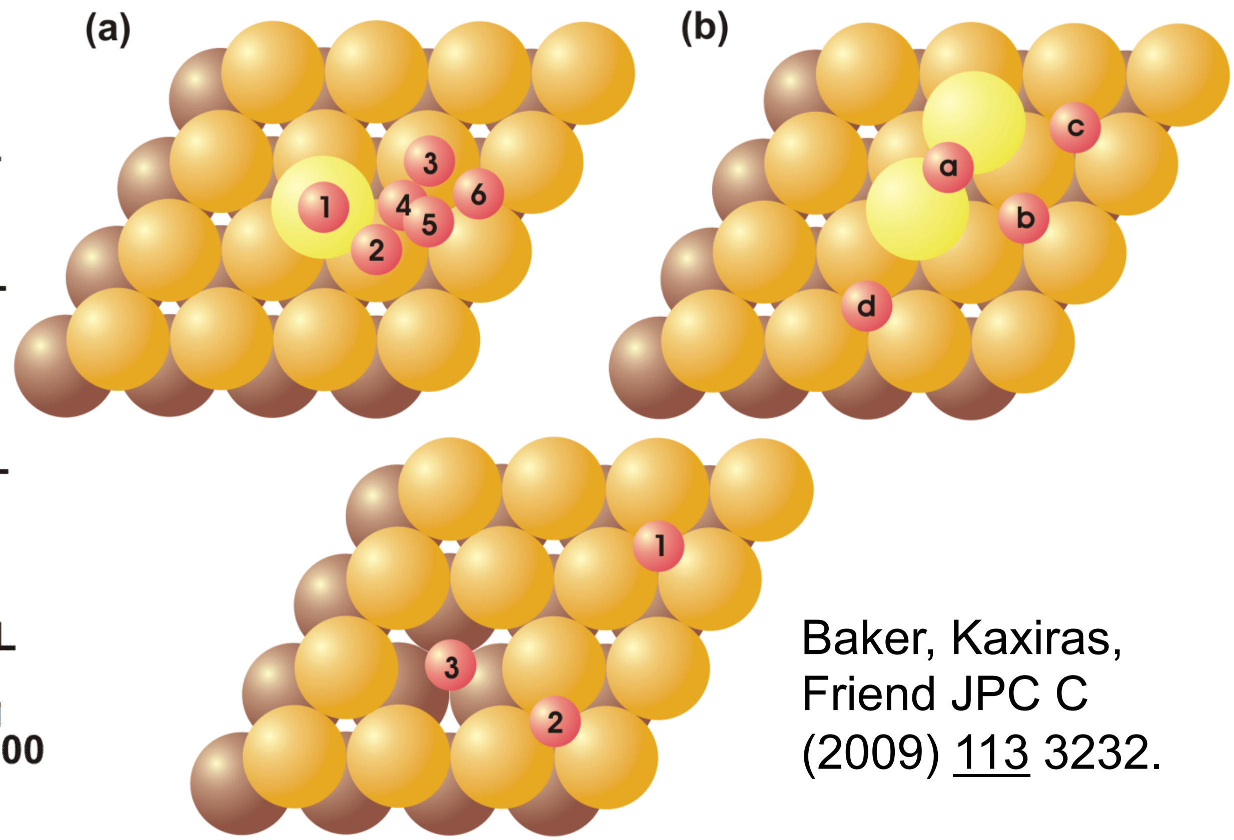
Heating leads to larger islands with local 2-D order

Local Bonding of O depends on Coverage: HREELS & DFT



FCC, 3-fold local coordination—ν (Au-O)=370-420 cm^{-1}

No fit



Baker, Kaxiras, Friend JPC C (2009) 113 3232.

Molecular Dynamics with DFT: understand local bonding of O species at higher coverage

Chemisorbed O

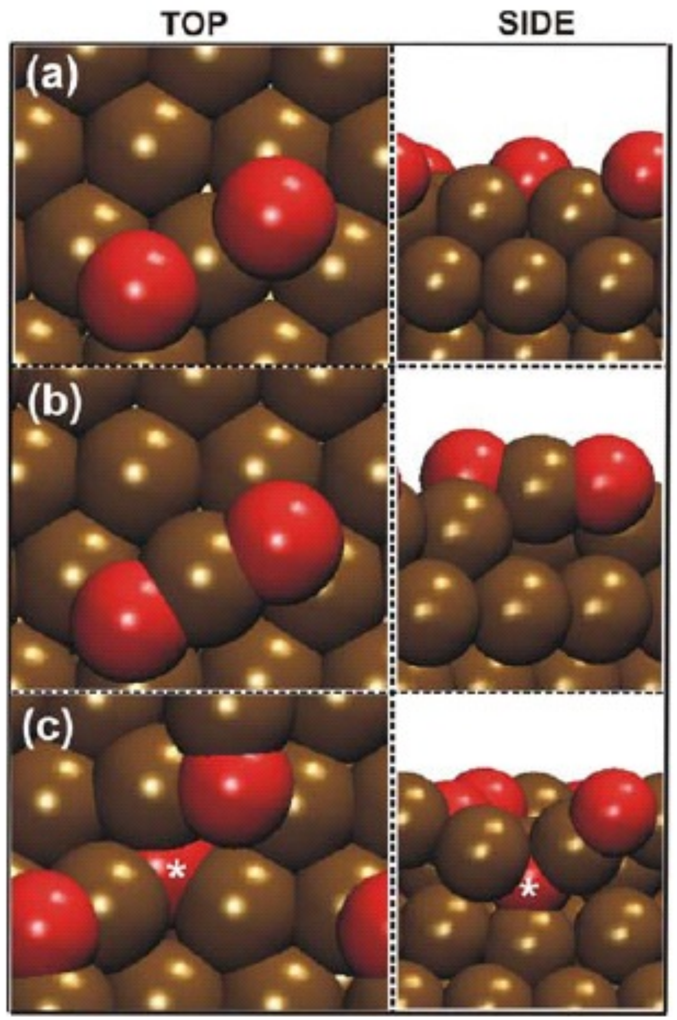
380 cm^{-1} peak

2-D "oxide"

380 & 560 cm^{-1} peaks

Subsurface "oxide"

380 & 560 cm^{-1} peaks

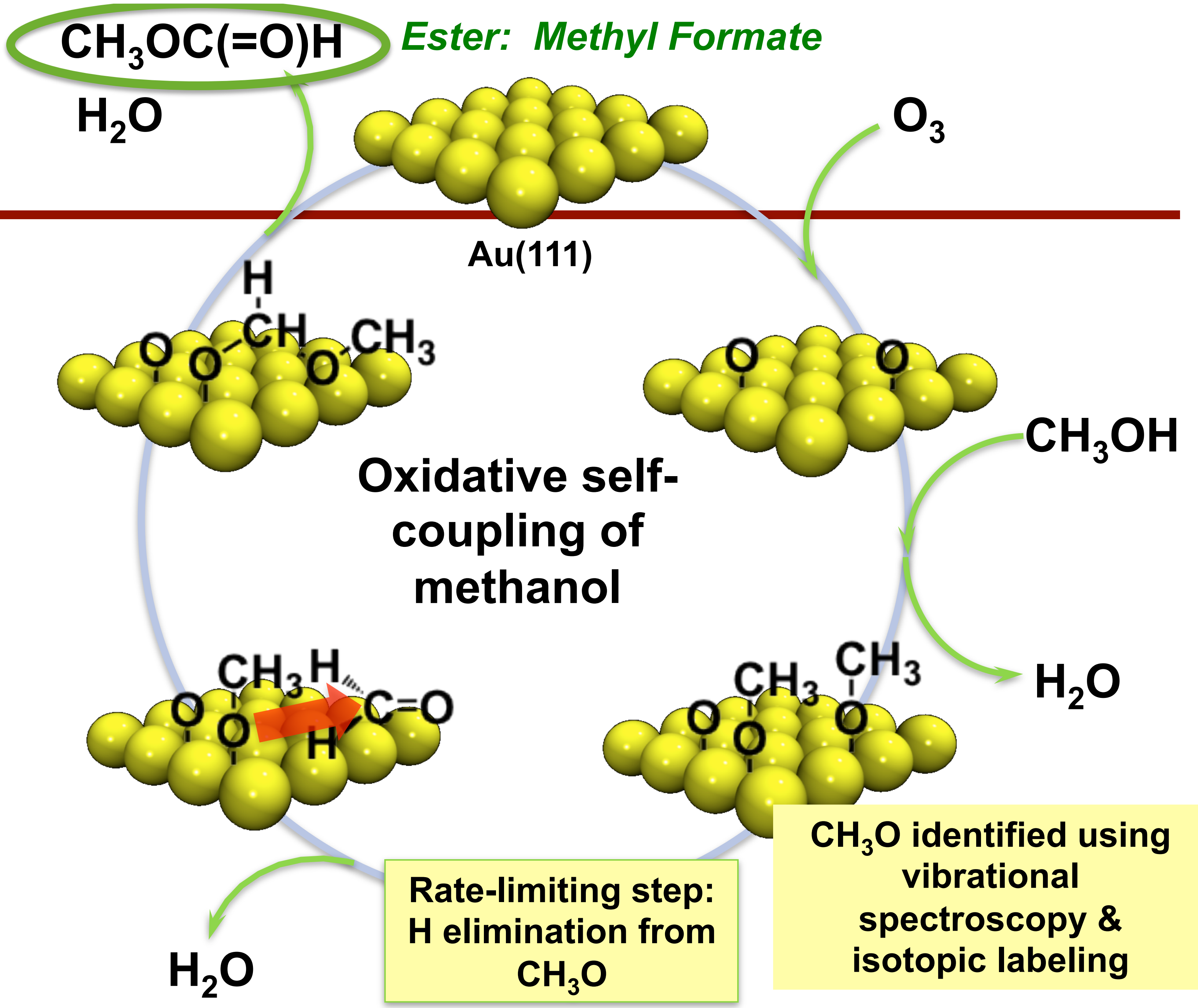


Low T, Low θ_O

Most reactive towards CO

High T, High θ_O

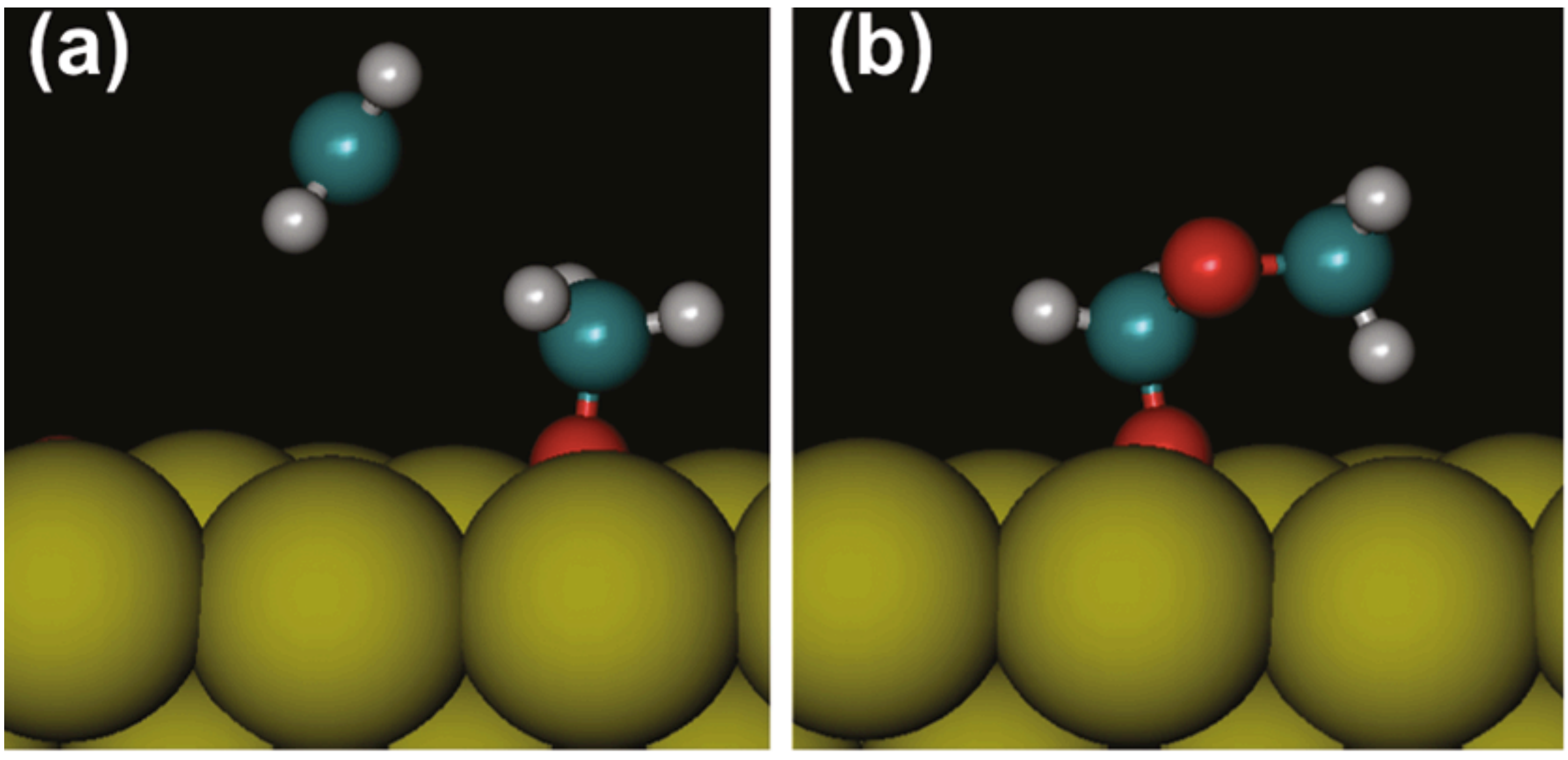
Baker, Xu, Liu, Kaxiras, & Friend, *J. Phys. Chem. C.*, **2009**, *113*, 16561-16564.



Xu, B., Liu, X., Haubrich, J., Madix, R. & Friend, C. Angew. Chem., Int. Ed. 48, 4206—4209 (2009).

DFT: Attack of $H_2C{=}O$ by CH_3O is spontaneous—no barrier

Adsorbed O facilitates last β-H elimination step; low barrier for transfer to Au (0.22 eV)



Xu, HaubrichBaker, Kaxiras, Friend, JPCC (2011) 115 3703-3708

Key Insights

- Loss of H from CH_3O ***determines rate***—adsorbed O, OH and CH_3O all can promote formaldehyde formation
- Au itself is unreactive, so O_{ads} determines reactivity
- Weak binding of key reactants, e.g. $H_2C{=}O$, OH, & H_2O, facilitates migration and rearrangement to preferred reaction geometry for coupling—key aspect of Au reactivity

High selectivity is important in reduction in energy cost using catalysis

- ***Increase selectivity*** —get the product you want with little or no waste

Example: Methanol oxidation on Ag or Au

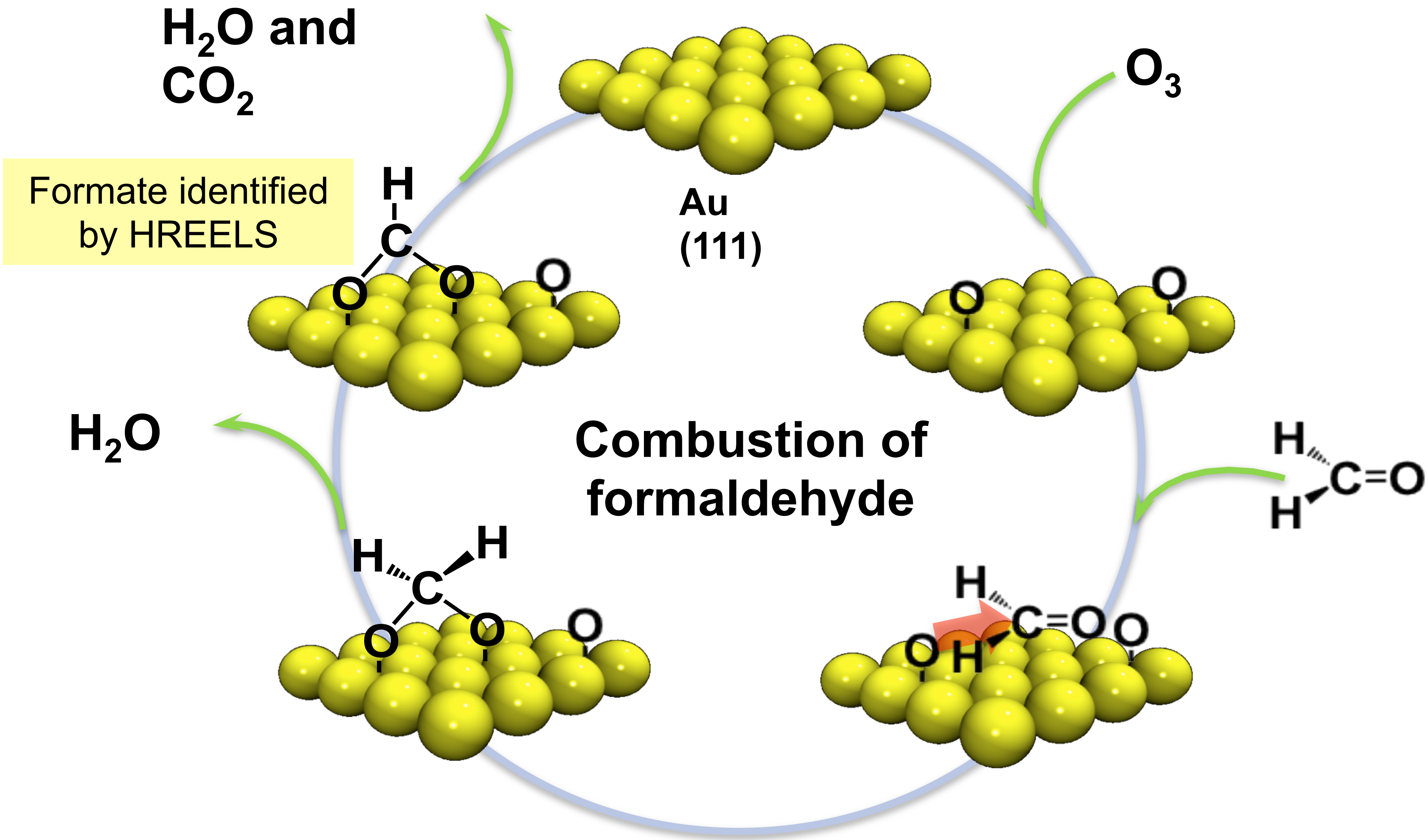
$CH_3O\text{-}C(H){=}O + 2\ H_2O$

$3\ CH_3OH + O_a \rightarrow H_2C{=}O + H_2O$

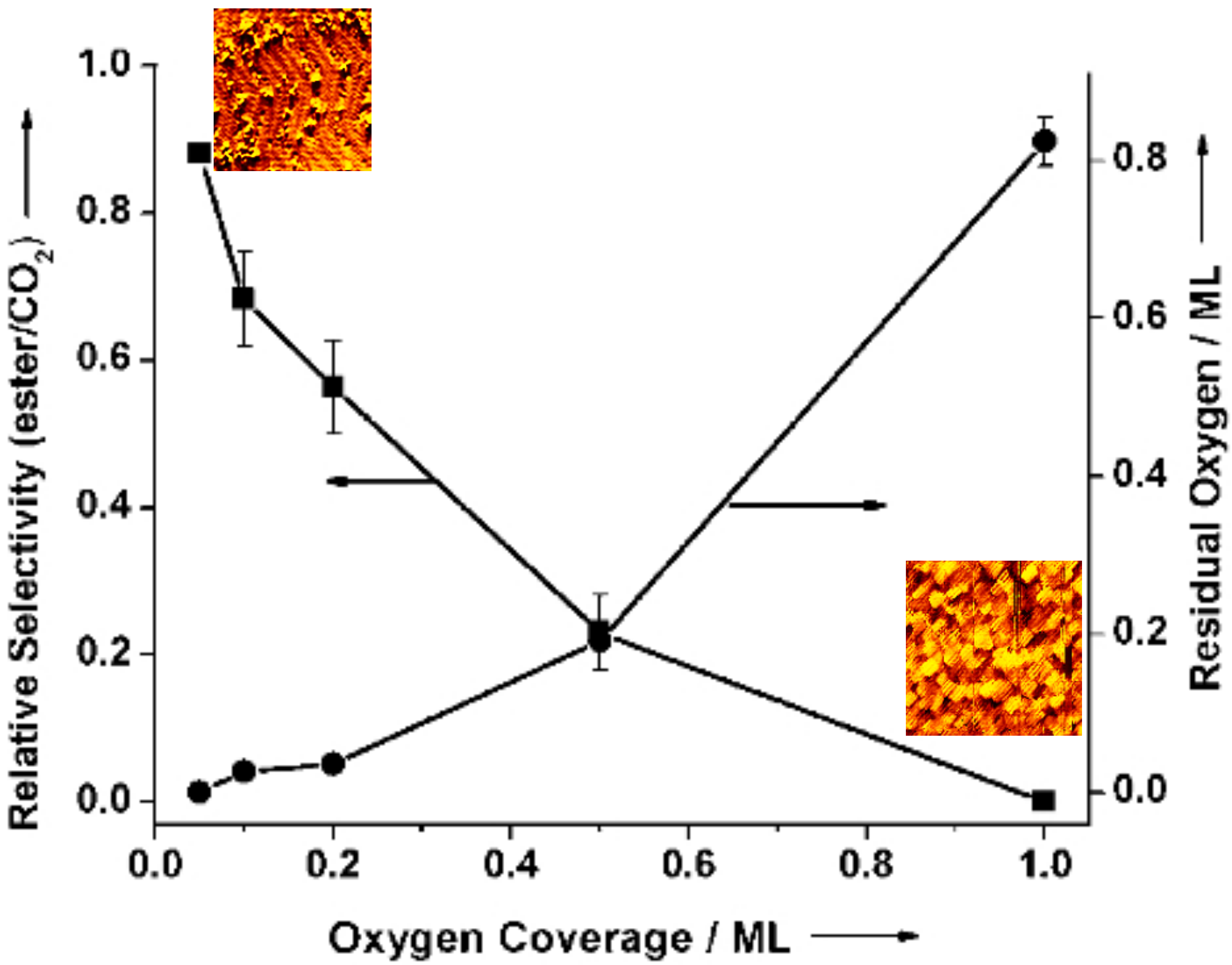
$CO_2 + 2\ H_2O$

Its all about ***kinetics!***

Formaldehyde Oxidation: Pathway for combustion/Reservoir of Formaldehyde



Principles governing Selectivity for methanol coupling



- "oxide" is less reactive
- secondary oxidation is fast relative to primary step
- Selectivity is low

O/Au(111) models reaction mechanism

Metallic Gold does **not** activate dioxygen. O_2

- Key challenge: delivering O to the surface

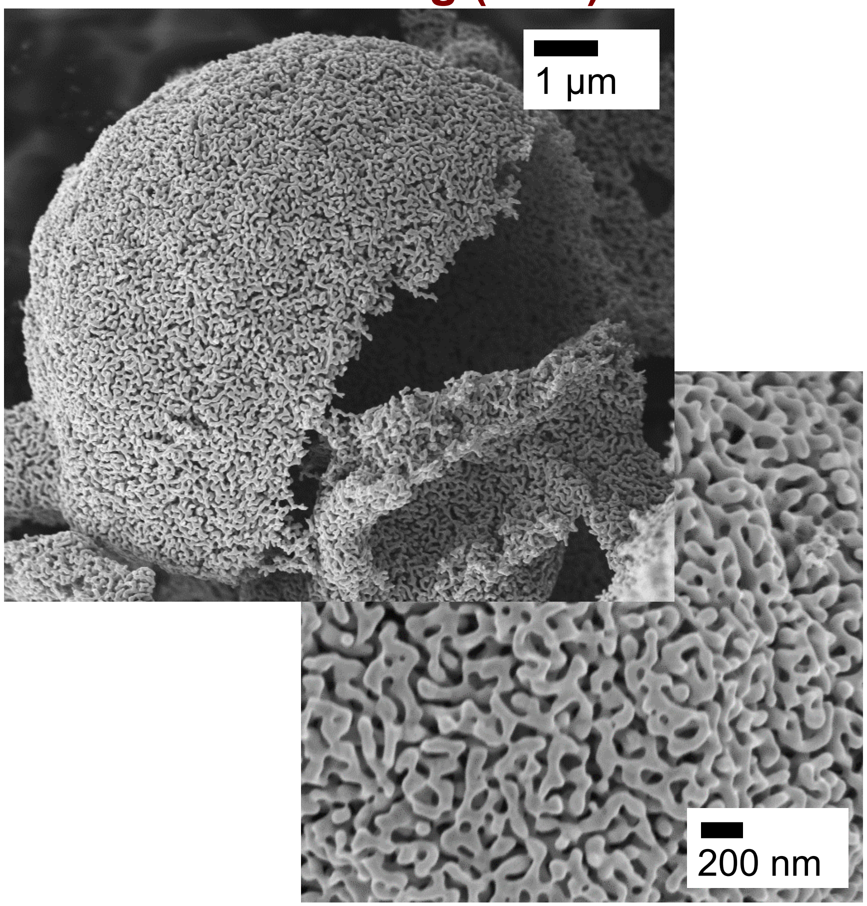
Metallic Silver activates O_2 at low temperatures by forming a peroxide-like species

Liu, X.; Madix, R. J.; Friend, C. M. *Chem. Soc. Rev*. **2008**, *137*, 2243.

Nanoporous Au Materials: Dilute Ag/Au alloys

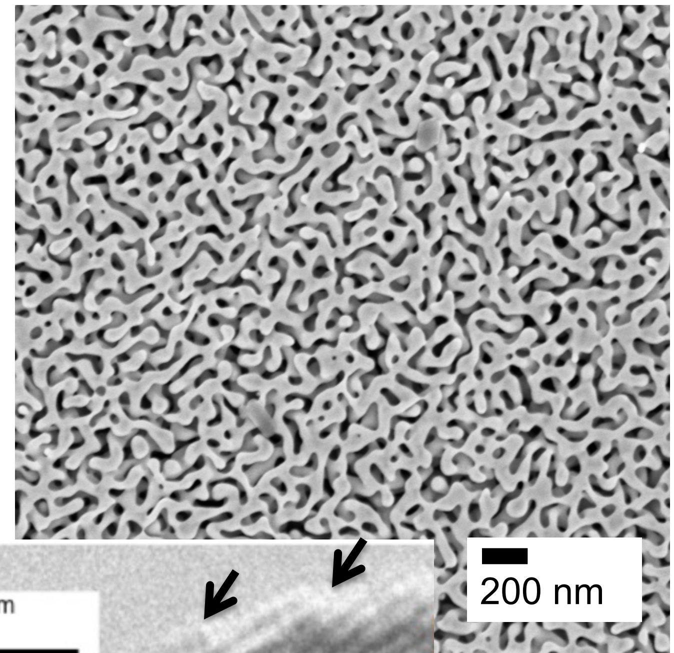
Nanoporous Au Microspheres

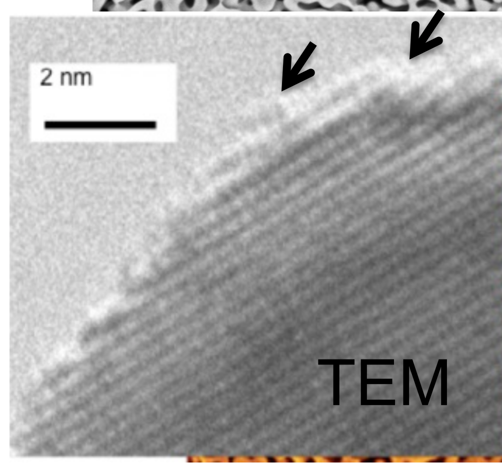
1-3 at% Ag (EDS)



Nanoporous Au Ingots

1-3 at% Ag (EDS)





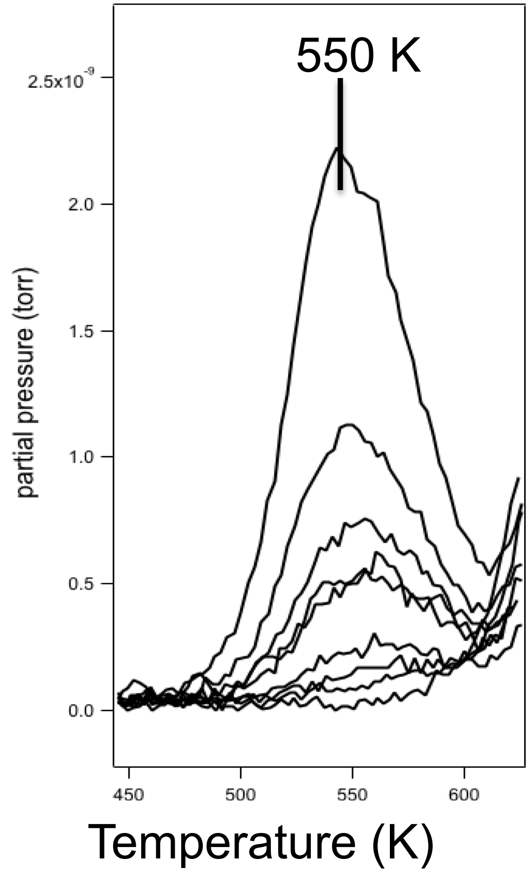
Highly crystalline

New catalyst architecture designed to reduce diffusion limitation

Unpublished work

Dilute Ag/Au alloys dissociate O_2— even in UHV

Nanoporous Au/UHV

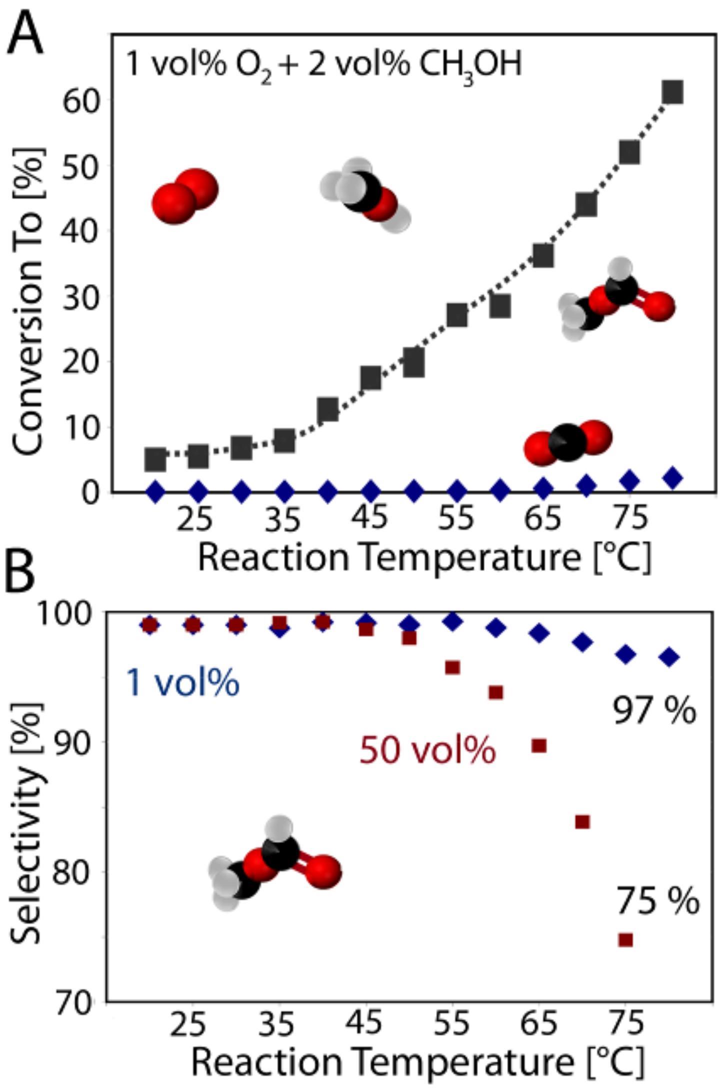


$2O_{ads} \rightarrow O_{2g}$ used to measure O uptake

Isotopic labelling

Unpublished results

Methanol oxidation on NP Au

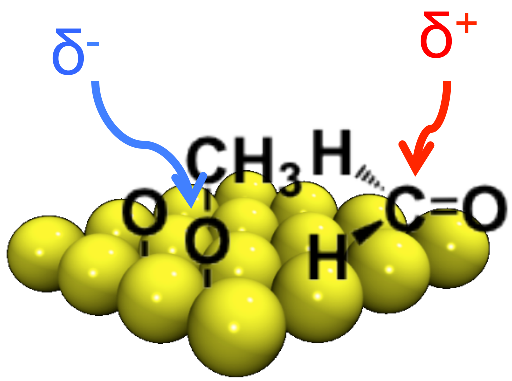


As predicted: esterification dominates at low O_2 partial pressures; no detectable $H_2C{=}O$

As predicted: Selectivity=ester:CO_2 decreases with T and O_2 partial pressure

Science, **2010**, *327*, 319-322

Possible role of theory: guiding principle for designing new reactions

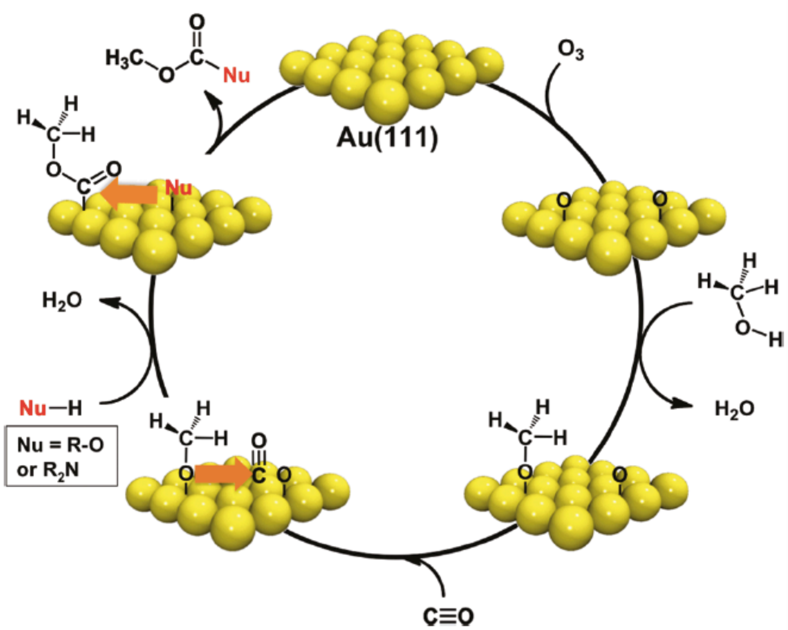


Electron distribution leads to reaction of negatively polarized species with positively charged one

Prediction: Any molecule with electron-deficient carbon should react with OCH_3 on O/Au

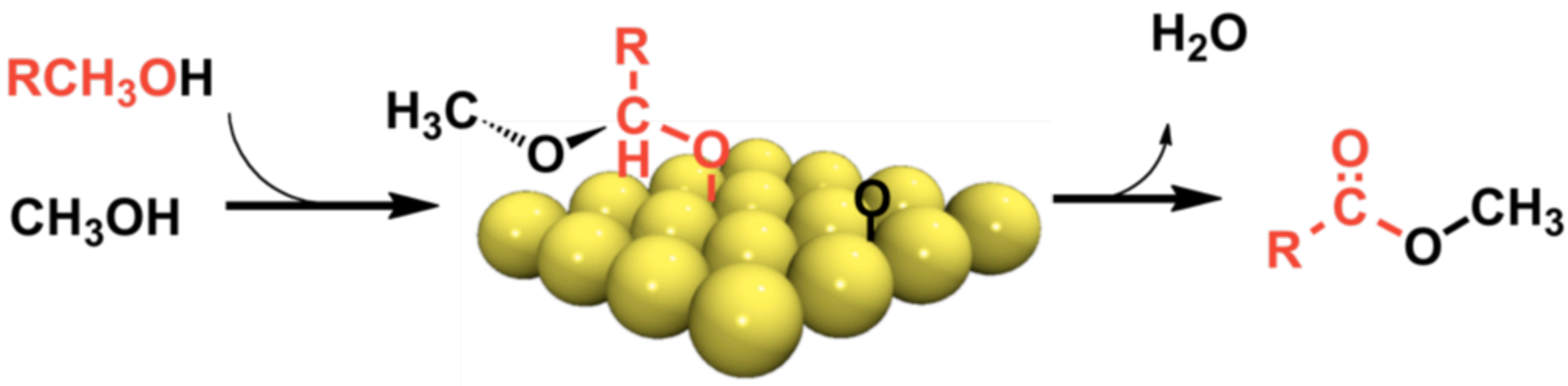
Surface Chemistry as a platform for reaction ***discovery***—new processes

Methanol carbonylation



Xu, Madix, Friend, JACS(2011);
dx.doi.org/10.1021/ja207389z

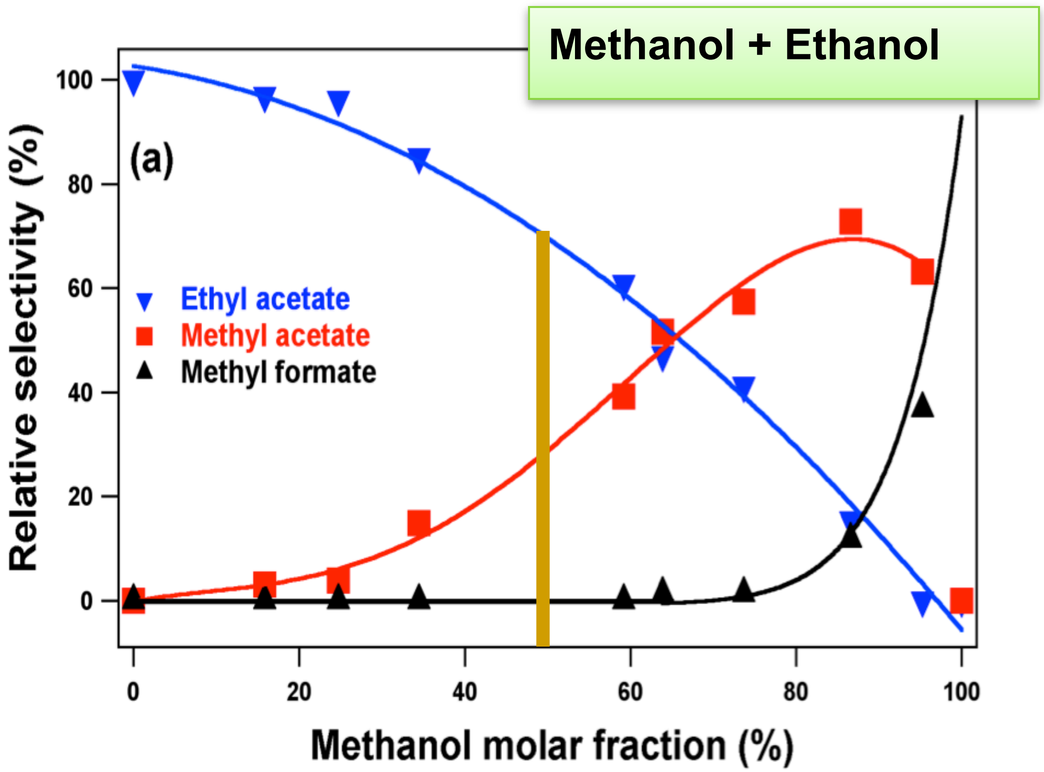
Tailoring coupling of higher alcohols: Illustrating importance of weak interactions



What controls selectivity for the different possible coupling pathways?

Xu, Friend, Madix, Chemical Sciences (2010) 1, 310-314, DOI: 10.1039/C0SC00214C.

Higher Alcohols: Displacement & β-H elimination are key factors

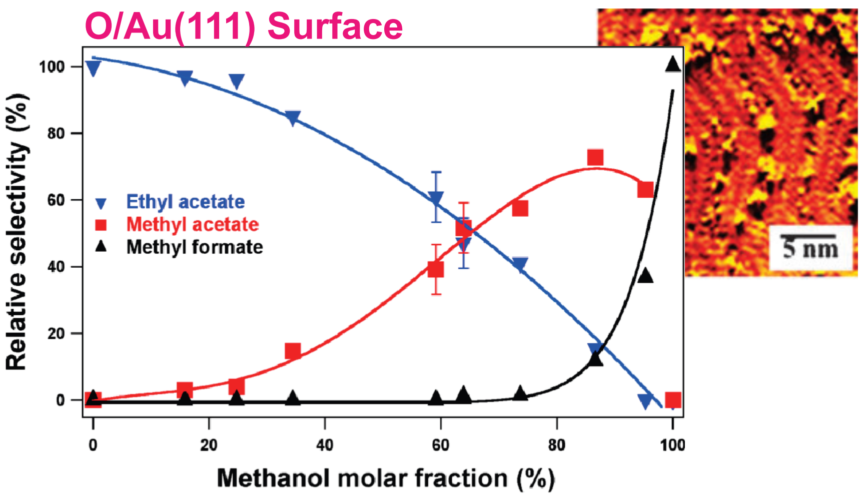


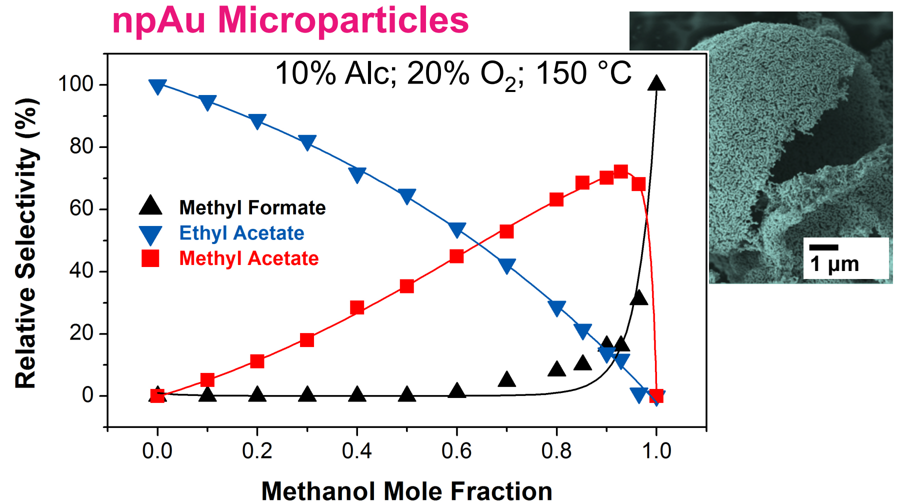
Relative surface coverage determined by equilibrium

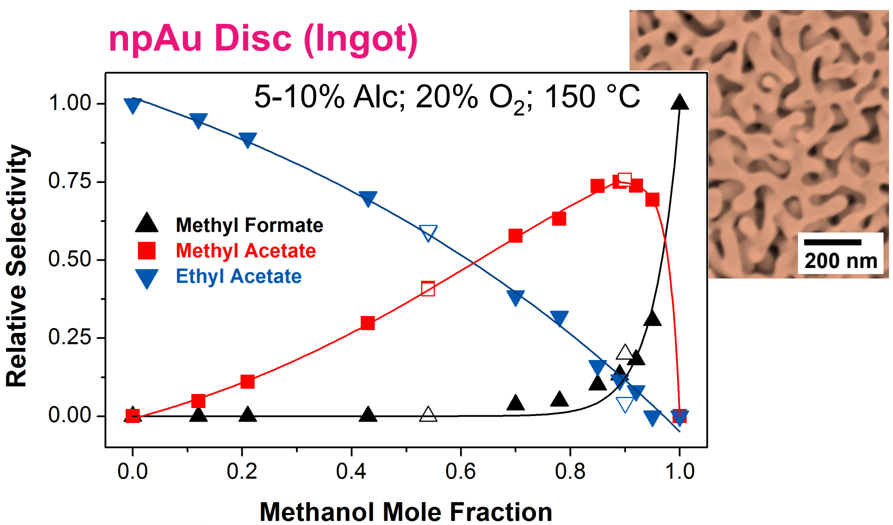
Rate of β-H elimination from $RCH_2O(ads)$: CH_3O reacts slowest

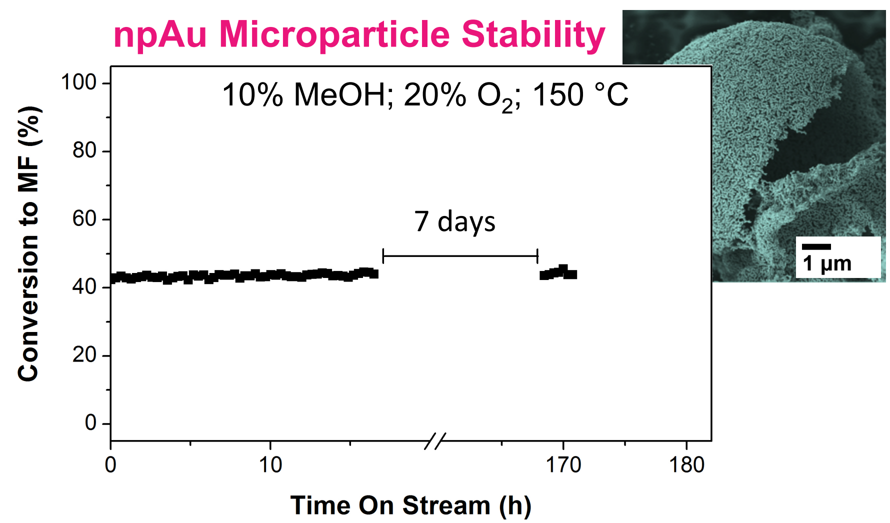
Xu, B., Madix, R.J. & Friend, C.M. JACS (2010).

From UHV to 1 atm Pressure: Catalytic Performance of npAu vs O/Au(111) similar even for complex envronments





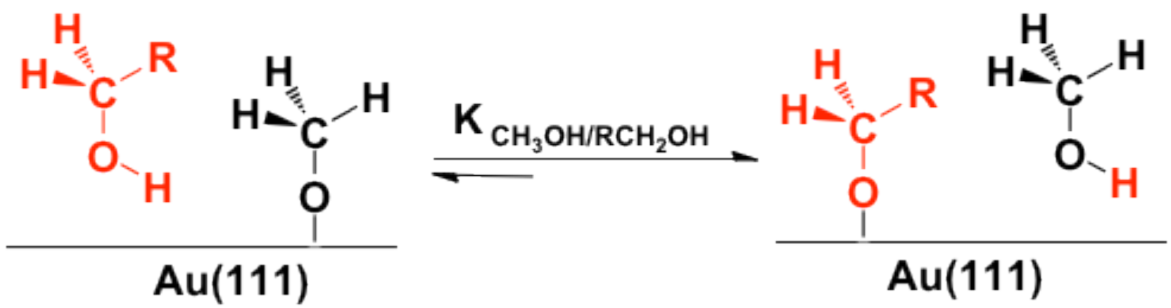




B. Xu et al. *JACS* **2010**, 132, 16571; B. K. Min et al. *J Phys Chem B* **2006**, 110, 19833; Unpublished work

Reactant binding determines competition for reaction sites

Relative surface concentration of intermediates determined by equilibrium:

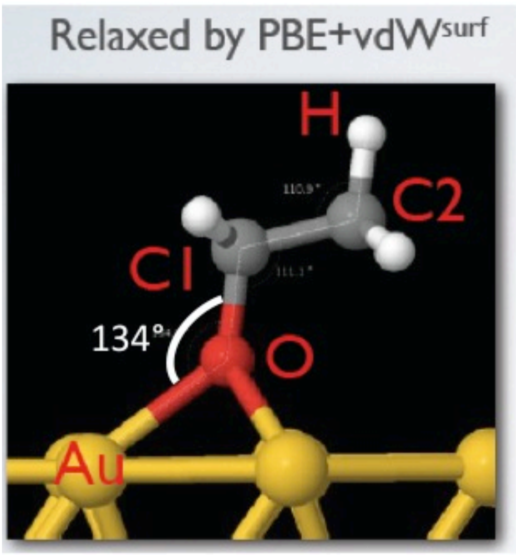


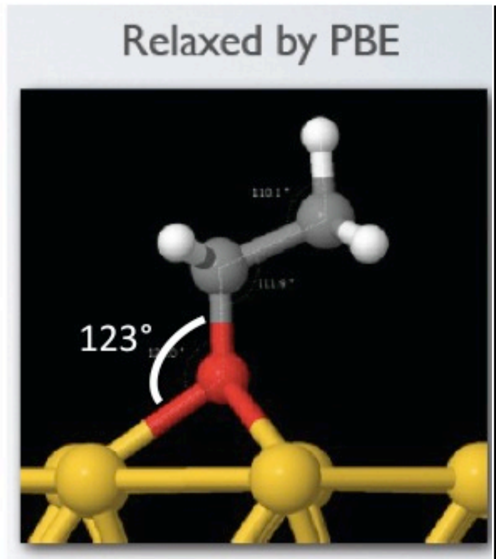
$$K = \frac{[CH_3OH][C_2H_5O]}{[CH_3O][C_2H_5OH]} = 8$$

Challenge for theory: Can competitive binding be predicted?

Xu, B., Madix, R.J. & Friend, C.M. JACS (2010).

van der Waal Interactions must be included to predict relative binding on Au





Adsorbate	E_b (eV) PBE	E_b (eV) PBE+ vdW	Difference due to vdW (eV)
CH_3O	1.15	1.29	0.14
CF_3CH_2O	1.11	1.41	0.30
CH_3CH_2O	1.38	1.64	0.28
1-$CH_3(CH_2)_3O$	1.33	1.80	0.47

JACS (2014), Siler, Rodriguez-Reyes, Madix, ***Liu, and Tkatchenko, FHI***

Binding energy scale established experimentally: Theory ongoing

Increasing surface stability

Conjugate Base	Gas Phase Acidity* (kJ/mol)
Butanoate	1451 ±8
Trifluoro acetate	**1351 ±12**
Acetate	1456 ±9
Formate	1445 ±9
Benzyl alkoxy	**1548 ±8**
Butoxy	1570 ±8
Ethoxy	1580 ±8
Trifluoro ethoxy	**1513 ±10**
Acetylide	1580 ±20
Methoxy	1597 ±6

Scaling relationships must go *beyond* simple atom-surface bond energies—roles of weak interactions & surface reconstructions must be evaluated

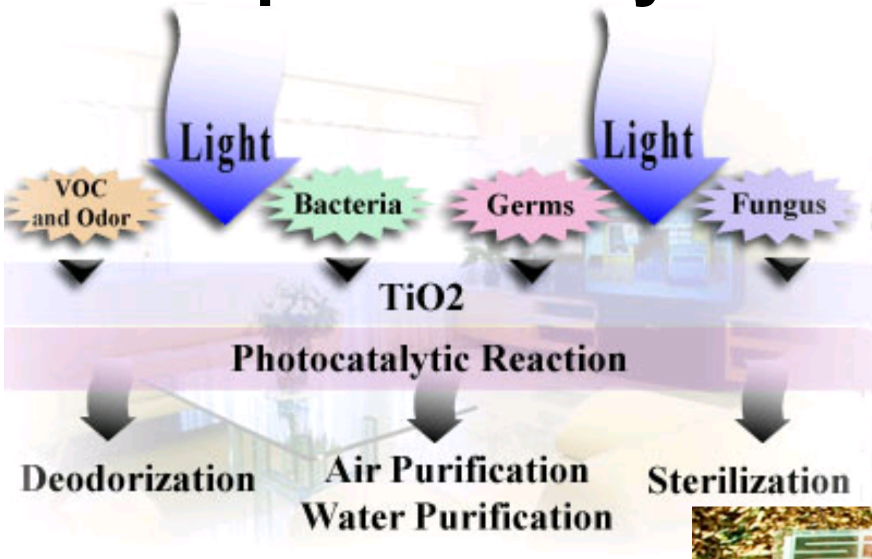
Rodriguez-Reyes, Siler, Liu,Tkatchenko, Friend, Madix, JACS (2014)

Fundamental studies provide understanding of catalysis

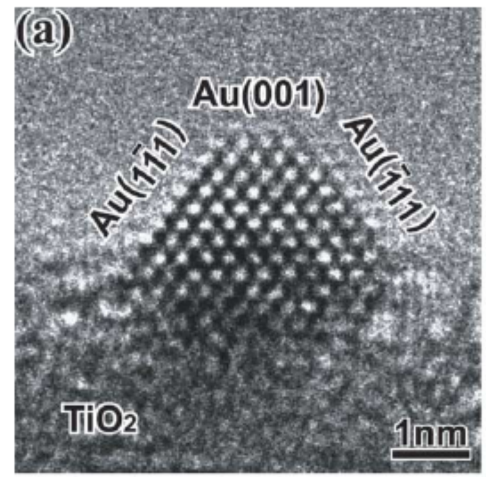
- O_{ads} is the reactive site for initiation of alcohol oxidation on Au (and Ag)
- Mechanism is determined using spectroscopy and modeled by DFT
- Van der Waal's interactions are key factor in determining selectivity in complex environments
- Fundamental studies guide reaction design

Photochemical oxidation of organics on TiO_2

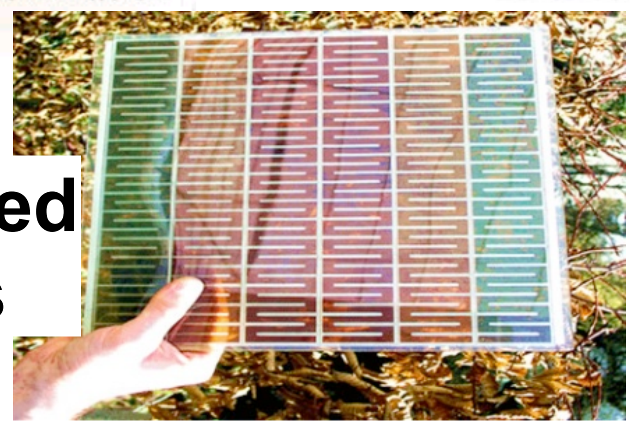
Titania is a catalyst and photocatalyst



Titania is a catalyst support material

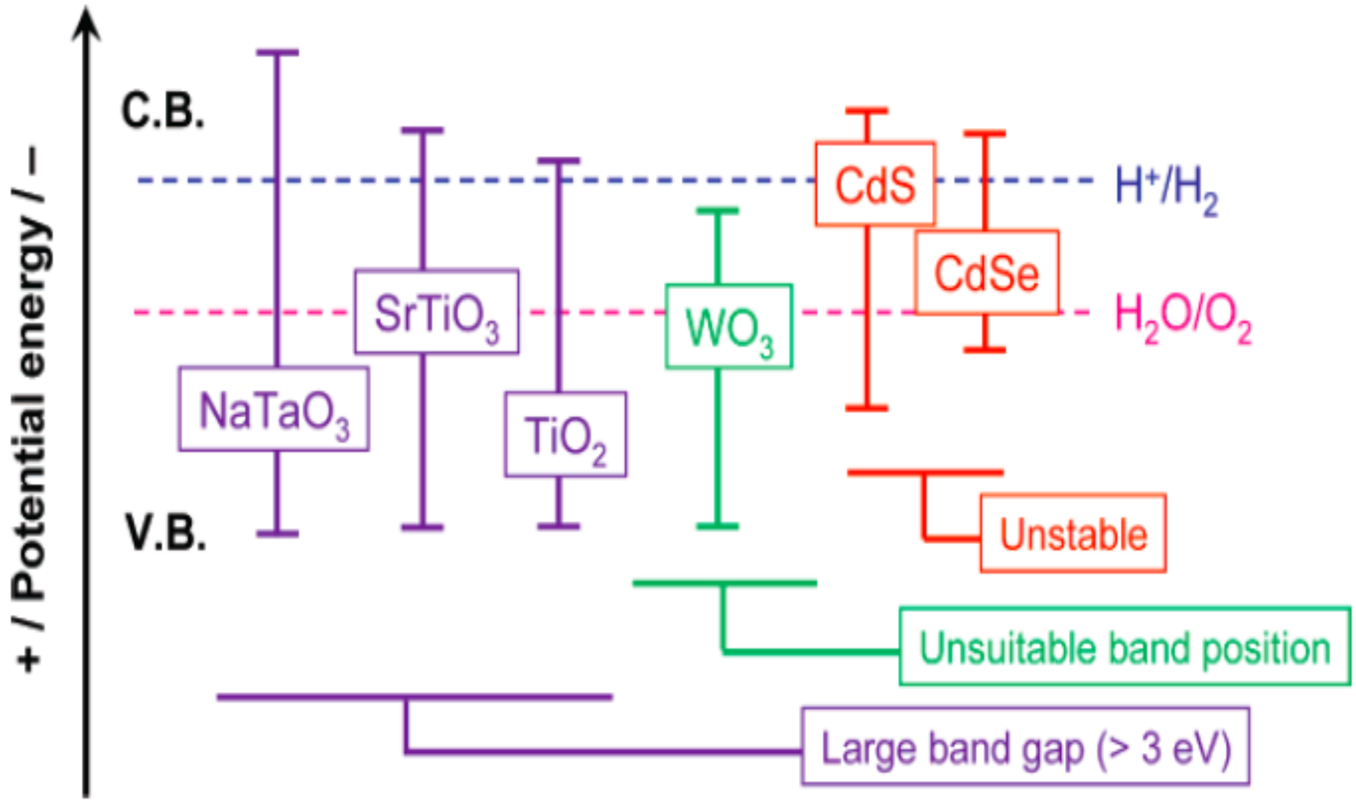


Dye Sensitized Solar Cells



Catalyst selection: Match energetics of reaction to band gap

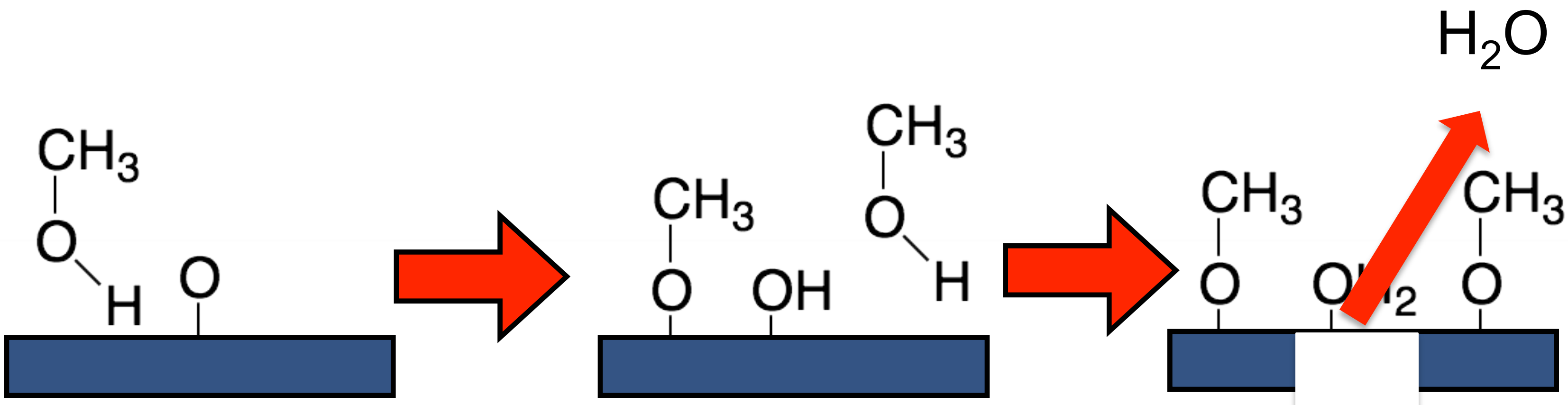
Thermondynamic considerations only—does not account for mechanism



K. Maeda, K. Domen, *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.

Methanol reacts with O adatoms to form methoxy on r-TiO_2(110)

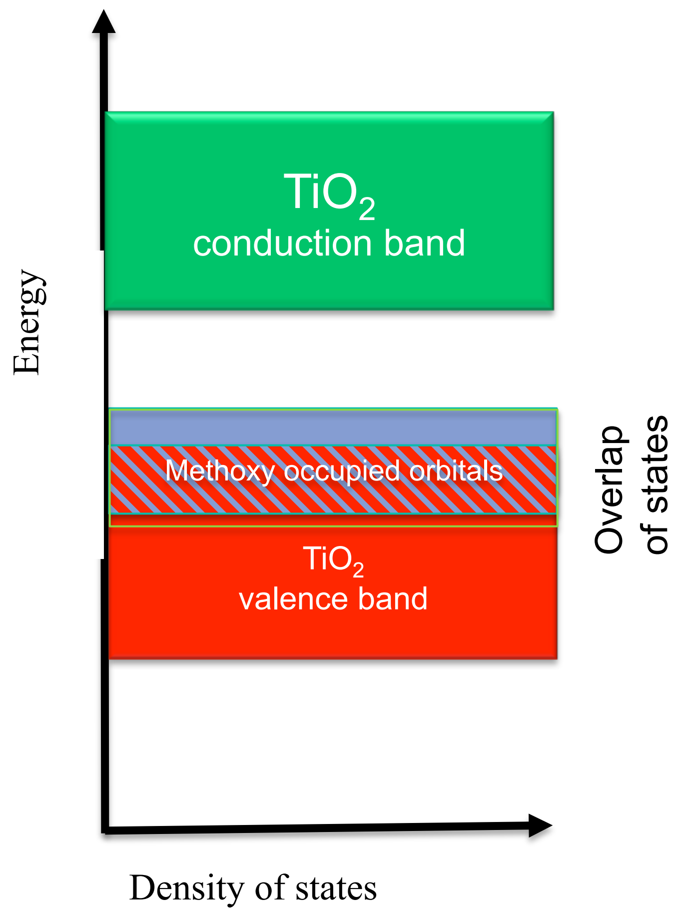
Methoxy—key intermediate—is formed thermally via reaction with O adatoms



Pure layer of methoxy created at RT—***no*** residual O_{ad}

K. Phillips, S. Jensen, M. Baron, S. Li, C. Friend, *JACS,* 2013 ASAP

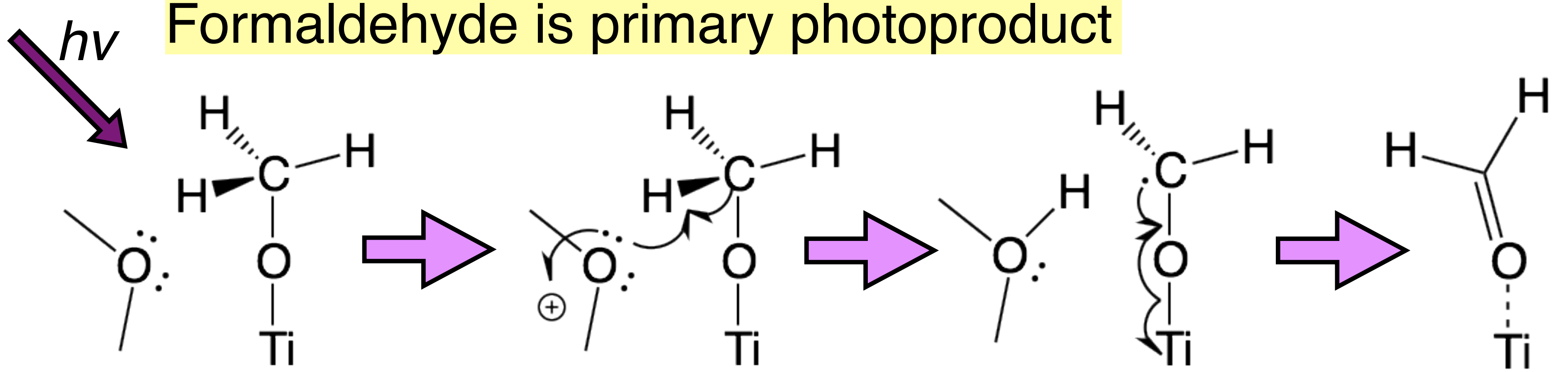
Schematic of valence structure including adsorbed methoxy



Excitation of electron-hole pair will also involve molecular states

Going beyond thermodynamic arguments: Photo-oxidation of methanol to formaldehyde

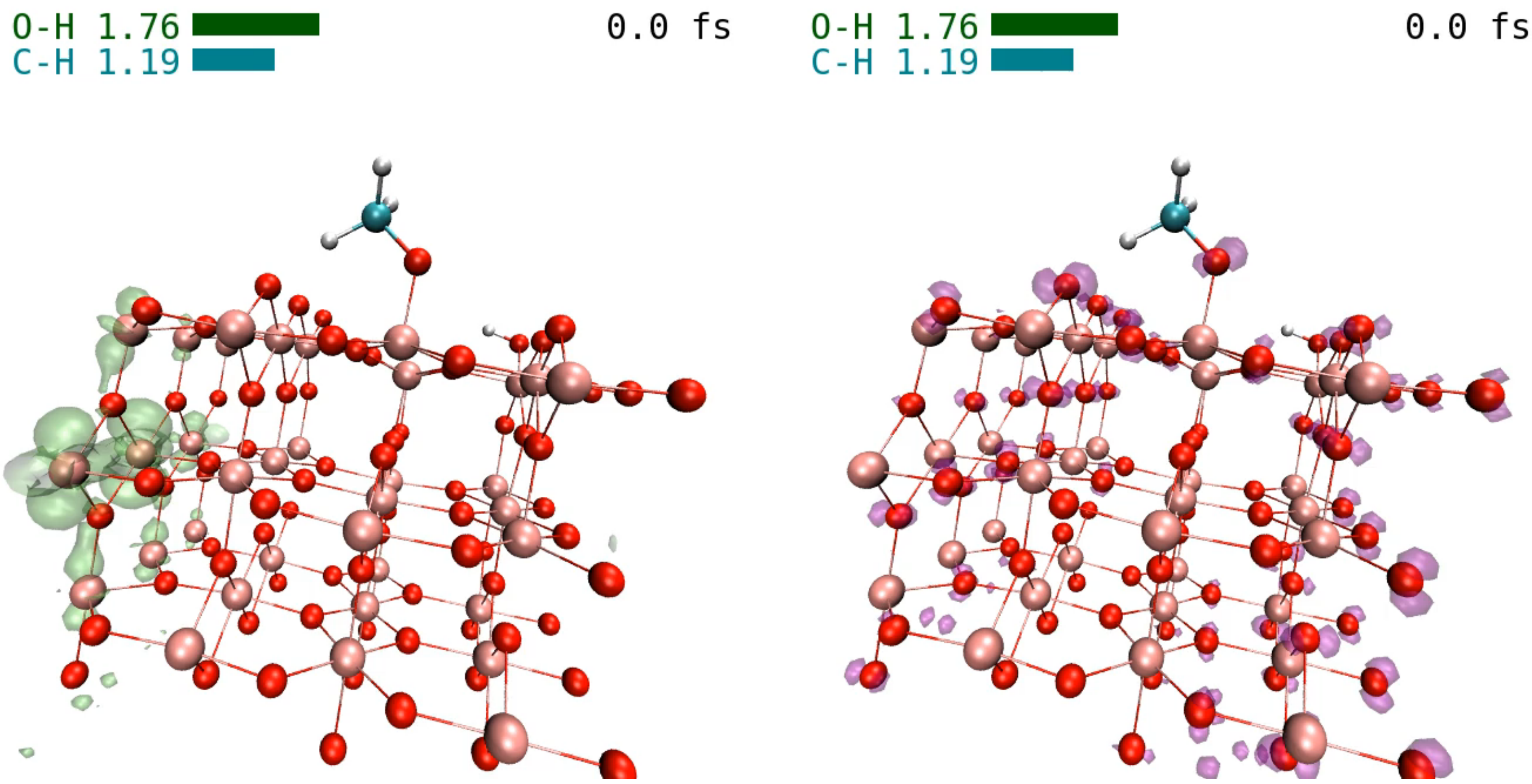
Formaldehyde is primary photoproduct



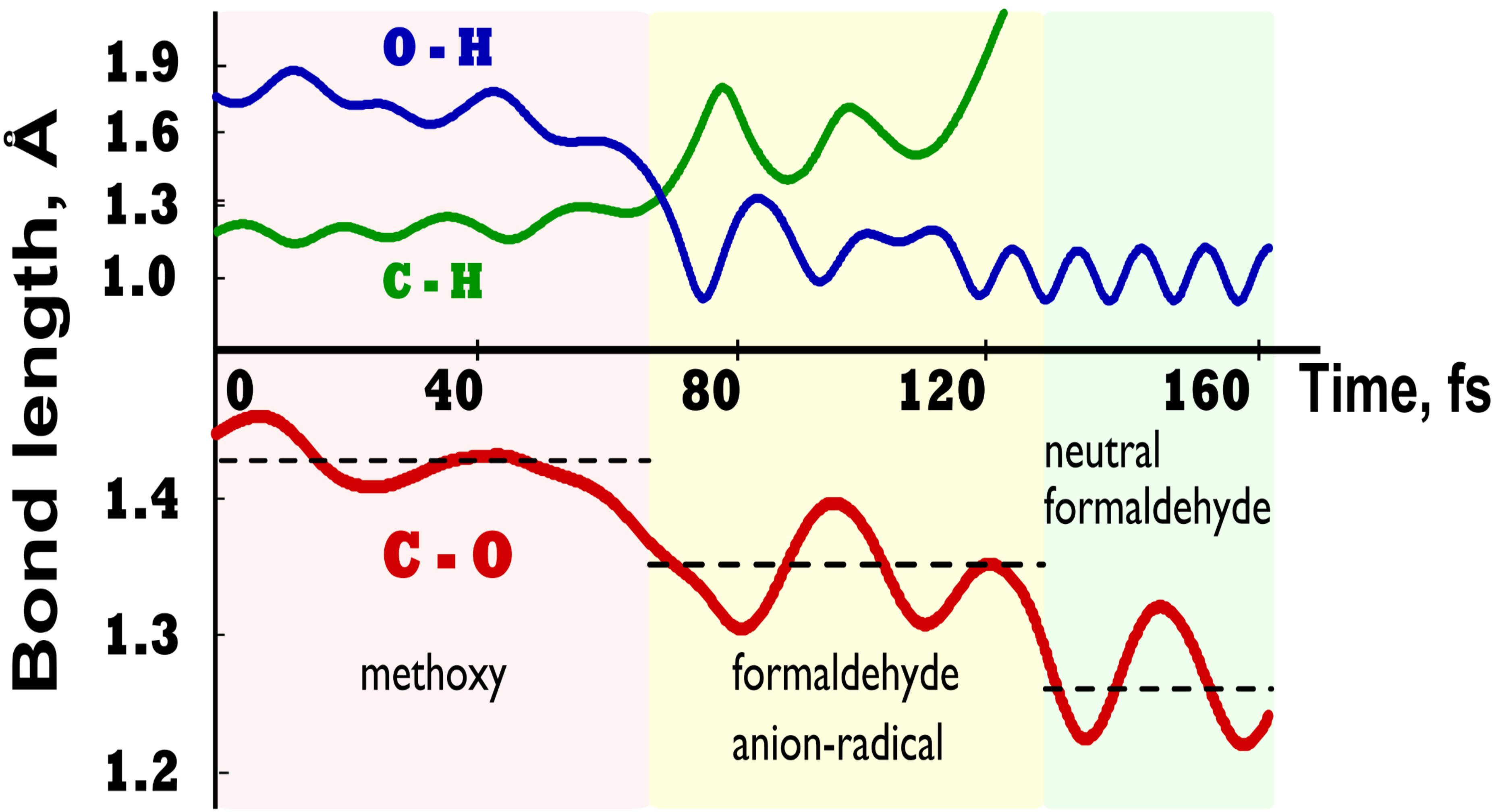
Henderson, etal. dx.doi.org/10.1021/jz201242k | J. Phys. Chem. Lett. 2011.

Theoretical treatment of photo-oxidation using TDFT
Collaboration with Tim Kaxiras, Grigory Koselov, Dmitry Vinichenko, and George Tritsaris

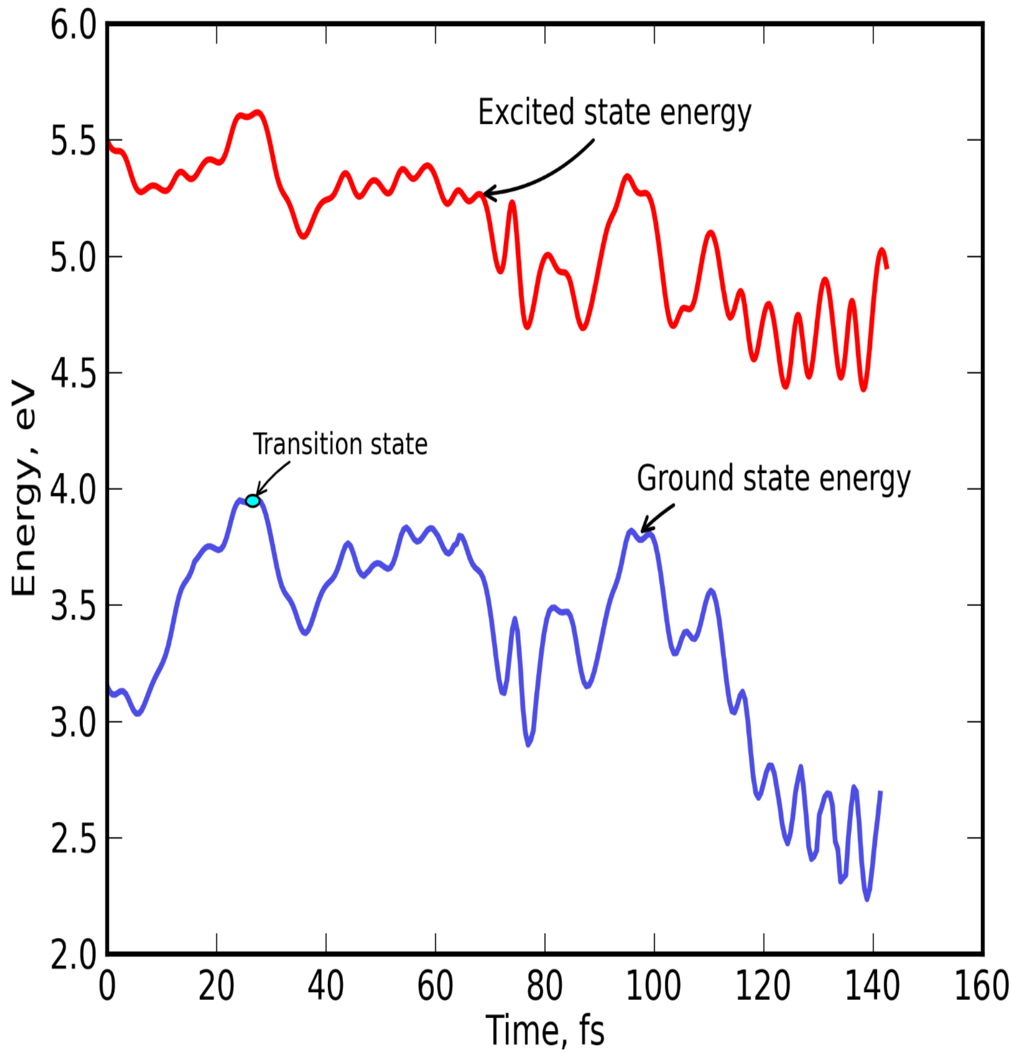
Overall Trajectory



Time evolution of Bond distances – rearrangement of electron density



Comparison of excited to ground state reaction path



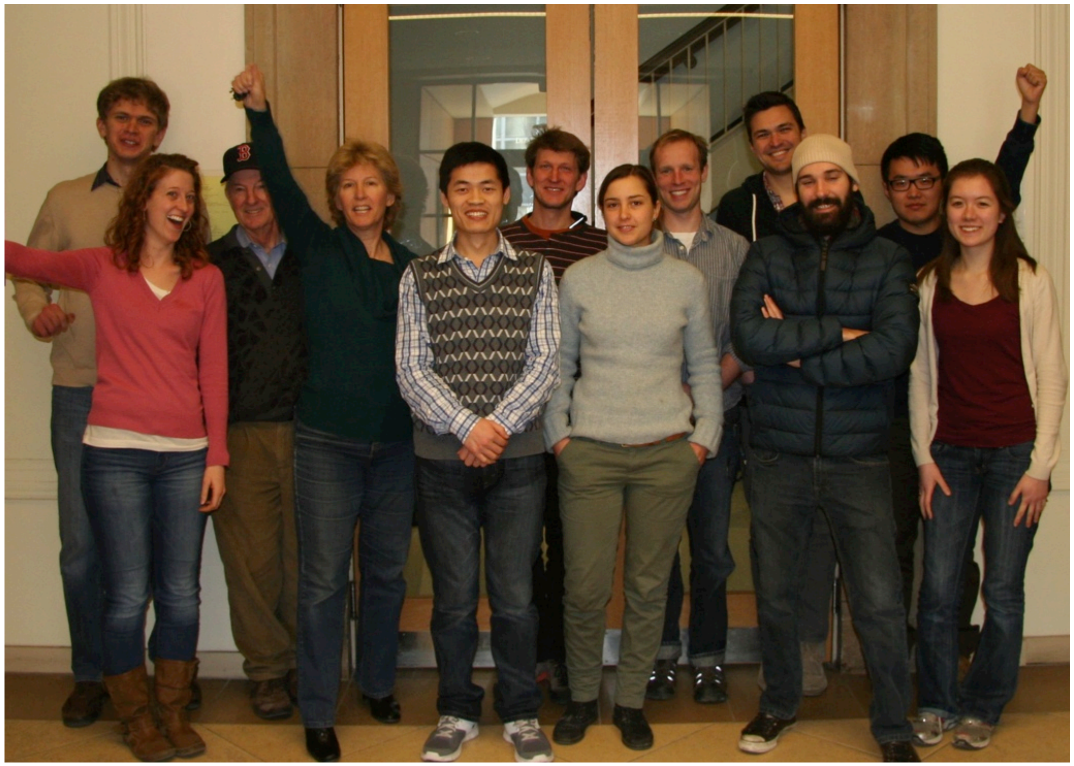
Energetics – almost strictly downhill on excited state PES; strongly uphill for ground state

Summary

- Molecular structure and reaction mechanisms are important in determining photo-reaction pathways
- Composition (defect) control is important to photochemical efficiency and selectivity
- Treatment of time evolution of excited states will provide better insight into mechanisms

Acknowledgements

Gold:
T. Baker
M. Bauemer (Bremen)
J. Biener (LLNL)
M. Biener (LLNL)
J. Haubrich
E. Kaxiras
X. Liu
R. Madix
M. Personick
M. Schmid
C. Siler
K. Stowers
L-C. Wang
A. Wittstock (Bremen)
B.-J. Xu
B. Zugic



Oxides:
K. Al-Shamery
M. Baron
L. Benz
P. Clawin
Till Cremer
J. Haubrich
S. Jensen
E. Kaxiras
G. Koselov
Beth Landis
K. R. Phillips
G. Tritsaris
D. Vinichencko

$$=NSF-CHE and NSF-DMR

Backup slides

Methodology: Self Consistent Field (SCF) Theory

$$\rho(\mathbf{r}) = \sum_{n} f_n |\phi_n(\mathbf{r})|^2$$

DFT:

$$H_{eff}[\rho]\phi_n(\mathbf{r}) \equiv (T + V_{ne} + V_{Coul}[\rho] + V_{xc}[\rho])\phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r})$$

$$\Phi_{ground} = \mathcal{A}|(\phi_1)^2 \ldots (\phi_{N_{occ}})^2|$$

$$\Phi_{exc} = \mathcal{A}|(\phi_1')^2 \ldots (\phi_{N_{occ}-1}')^2 (\phi_{N_{occ}}')^1 (\phi_{N_{occ}+1}')^1$$

Primes mean orbital relaxation!

$$\Phi_{exc}^1 \rightarrow \rho_{exc}^1 \rightarrow H^1_{exc} \rightarrow \Phi_{exc}^2 \rightarrow \ldots \text{self-consistency}$$

Method: Ehrenfest dynamics

Electron dynamics:

$$i \partial \phi_n(t)/\partial t = H_{exc}[\rho](t)\phi_n(t)$$

Ion dynamics:

$$M_J \partial^2 R_J/\partial t^2 = \langle F_J \rangle = -\nabla_{R_J} V_{KS}^J[\rho(t)](R),$$

All equations discretized in 10 attoseconds time steps